Li-ion Batteries: Electric Cars

Amy L. Prieto
CSU

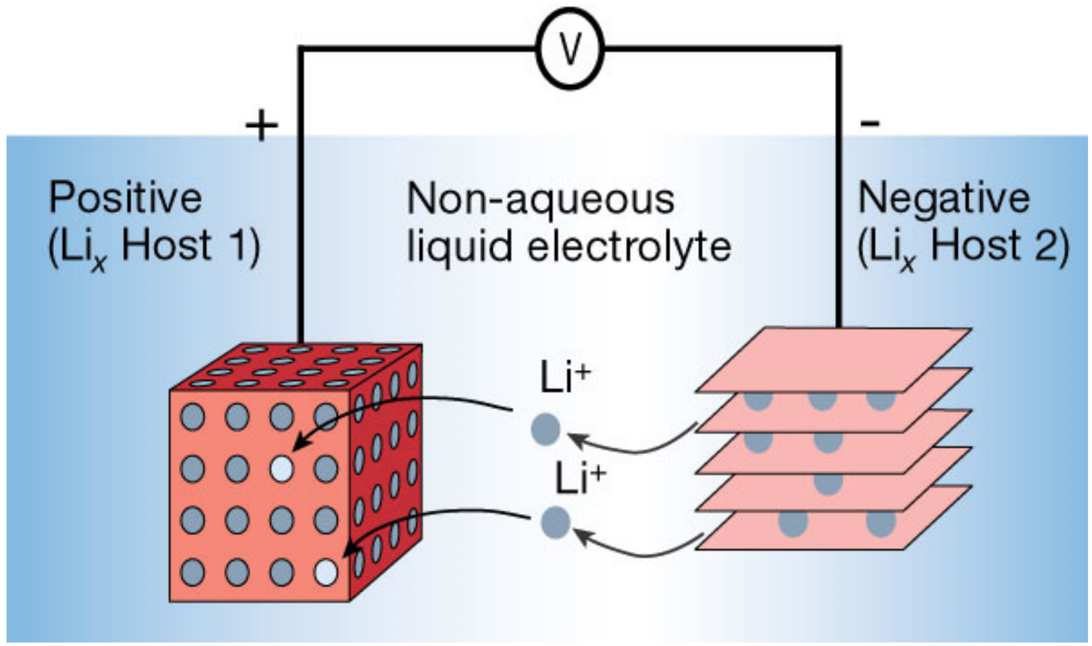
Tesla Roadster

0-60 MPH in 3.9 seconds

“244 miles” on a single charge

6,831 Li-ion cells = $36,000 replacement cost

Intercalation Chemistry



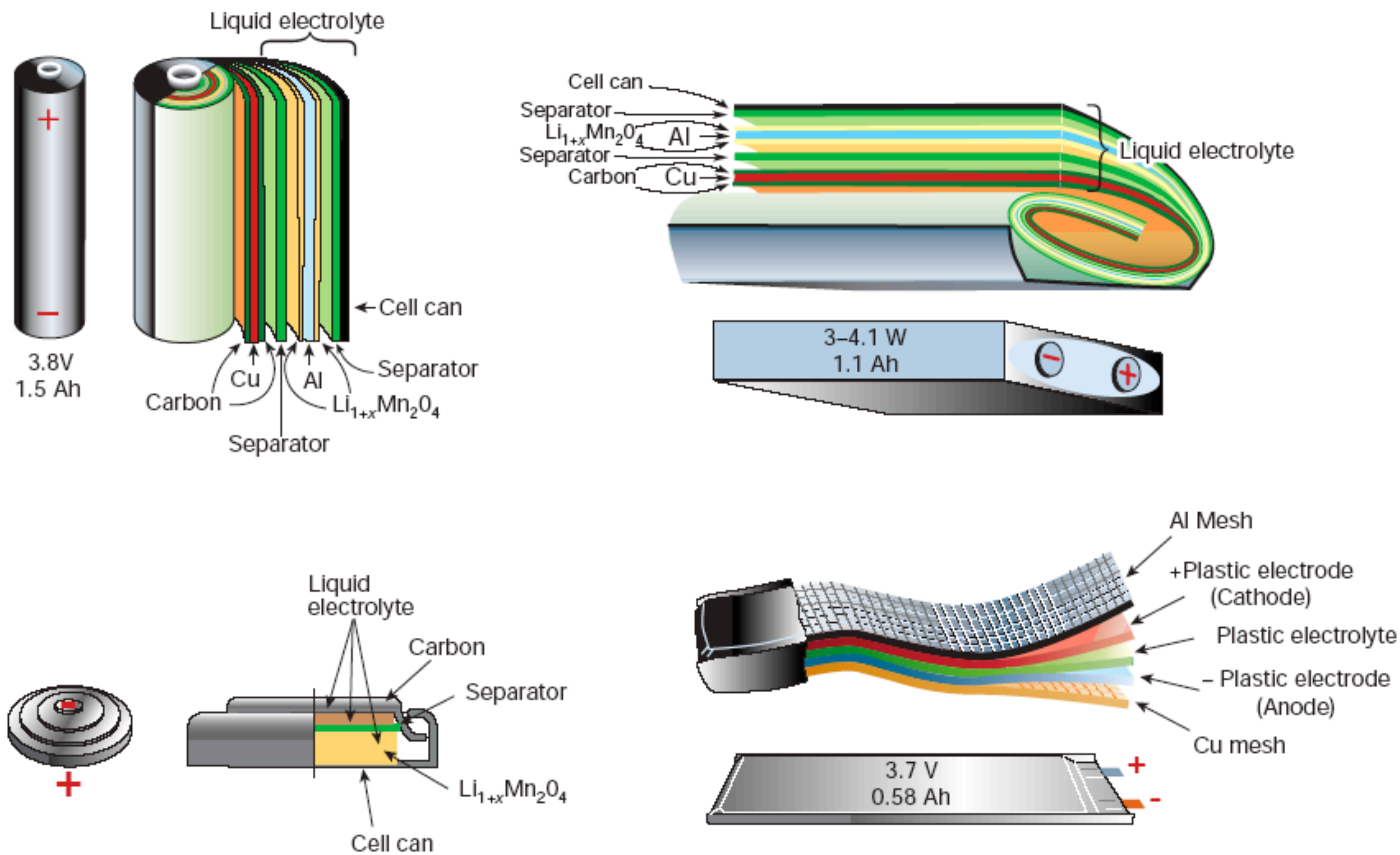
Limitation to Charging/Discharging Rates:

- diffusion of Li^+ into electrodes
- diffusion of Li^+ *between* electrodes

The problem of diffusion *between* the two electrodes has yet to be solved

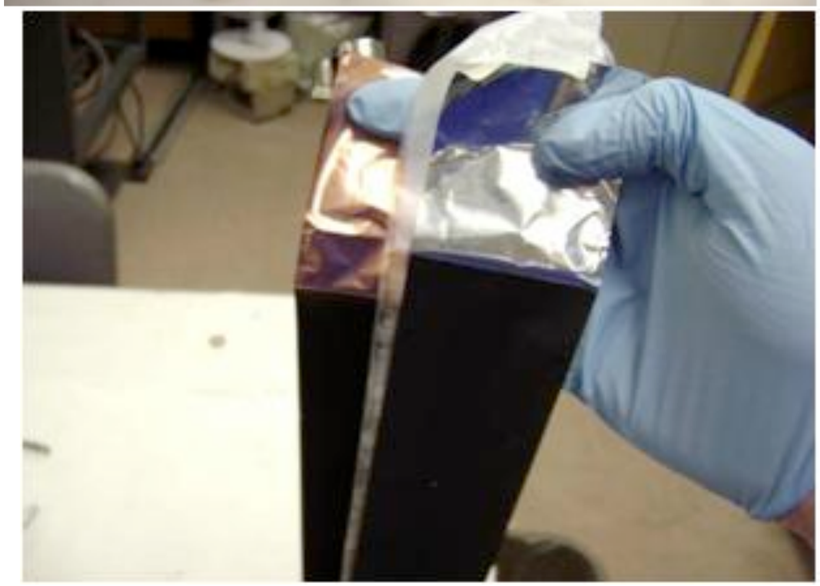
Tarascon, J.M. *et al. Nature*, **2001**, *414*, 359
Li, N., Martin, C.R., Scrosati, B. *J. Power Sources* **2001**, *97-98*, 240

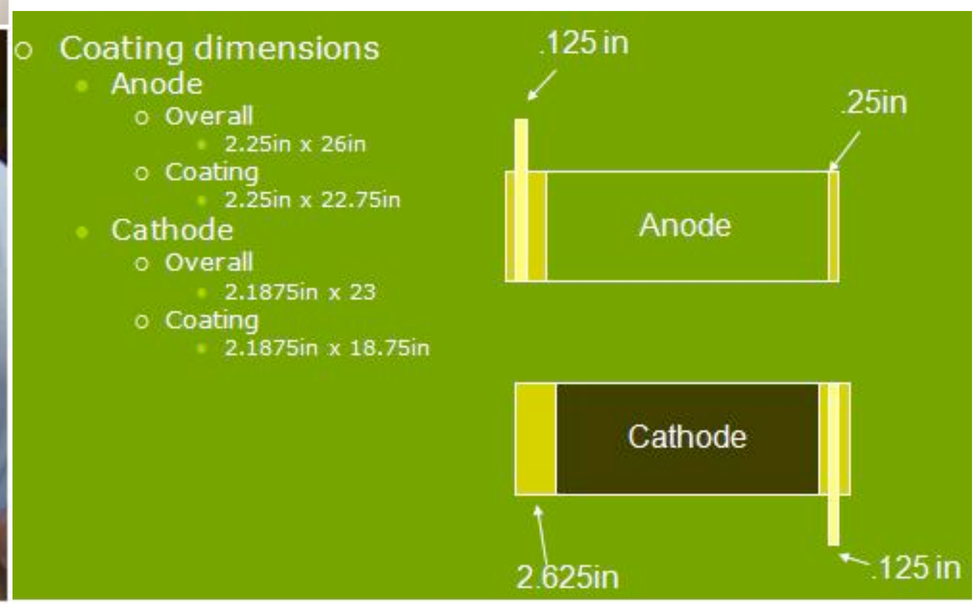
Common Battery Architectures



Tarascon, J.M., Armand, M. *Nature* **2001**, *414*, 359

Hand Made Batteries





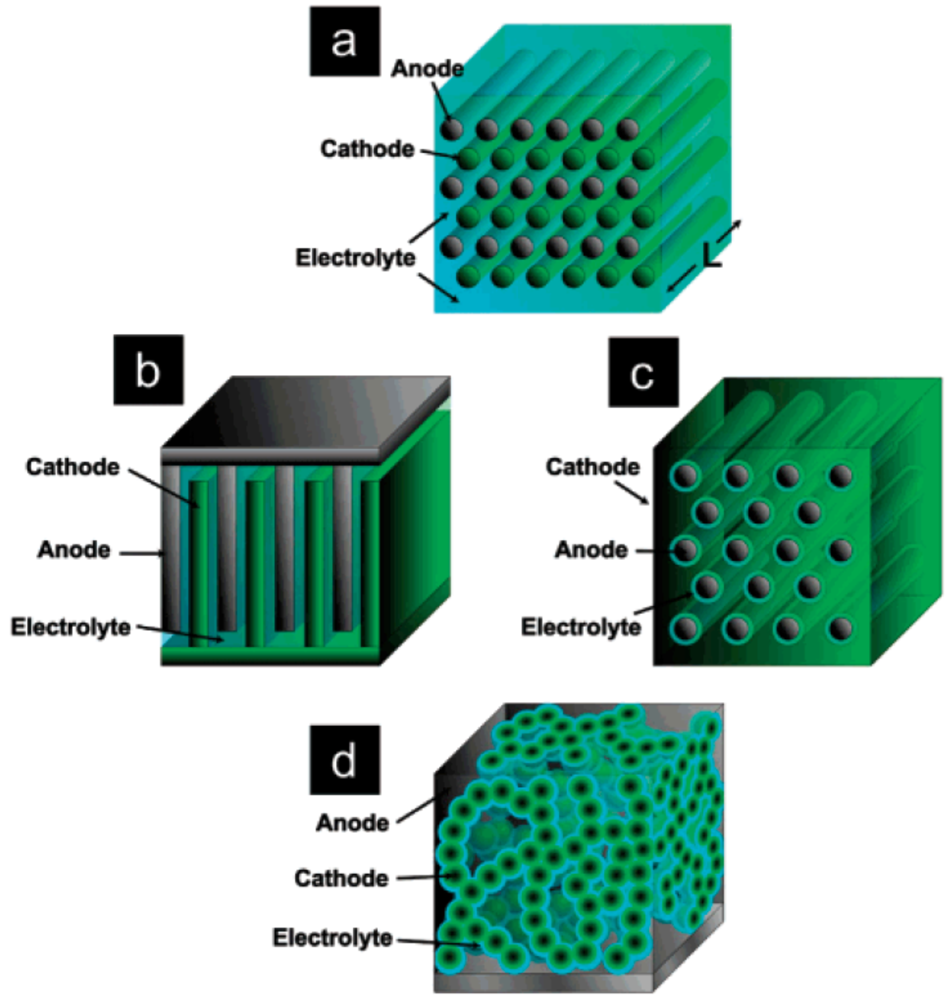
How to Make a 3D Battery

$$Power\ Density \propto \frac{Voltage \times Lithium\ ion\ conductivity \times Surface\ area}{Lithium\ ion\ transport\ length}$$

- **High surface area electrodes**
- **Short diffusion lengths between electrodes**

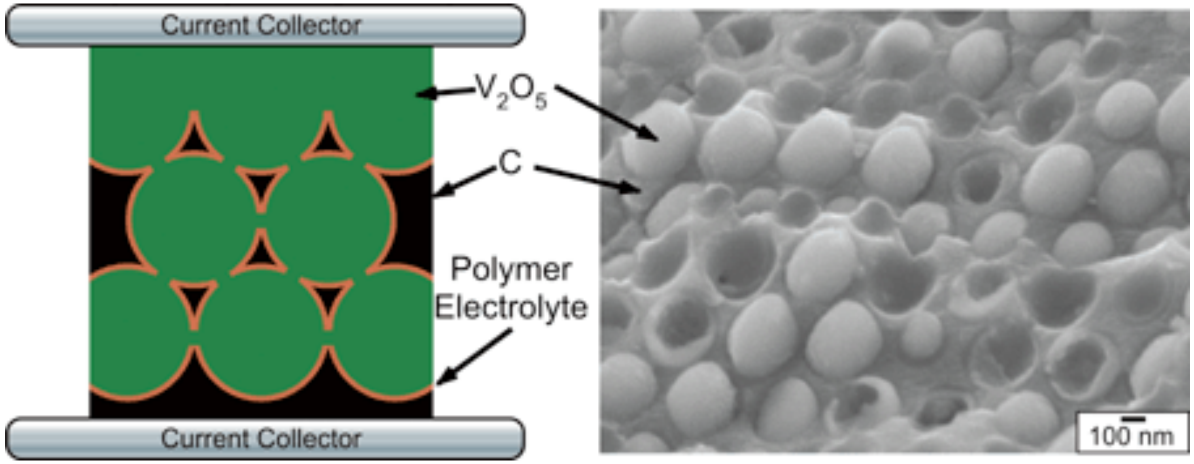
1. **Shape**
2. **Fabrication methods (cathode/electrolyte/anode)**
3. **How are you going to make electrical contact to each electrode?**
4. **How will you prevent shorting?**

Three Dimensional Battery Architectures

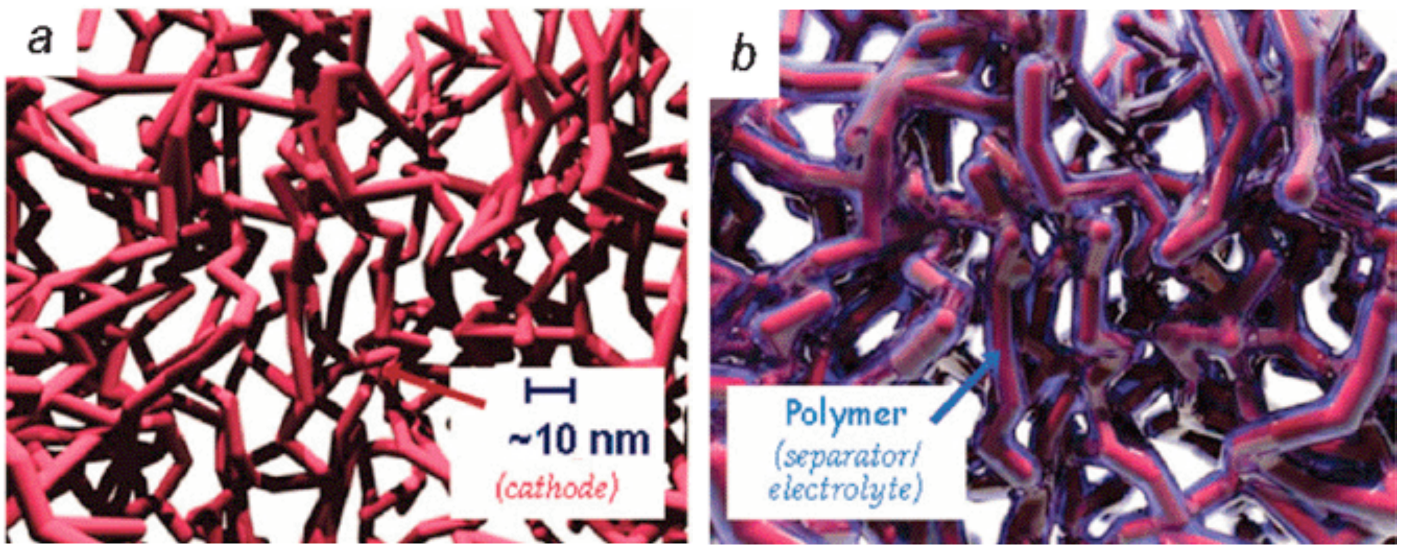


Rolison and Long, *Chemical Reviews*, **2004**, *104*, 4467

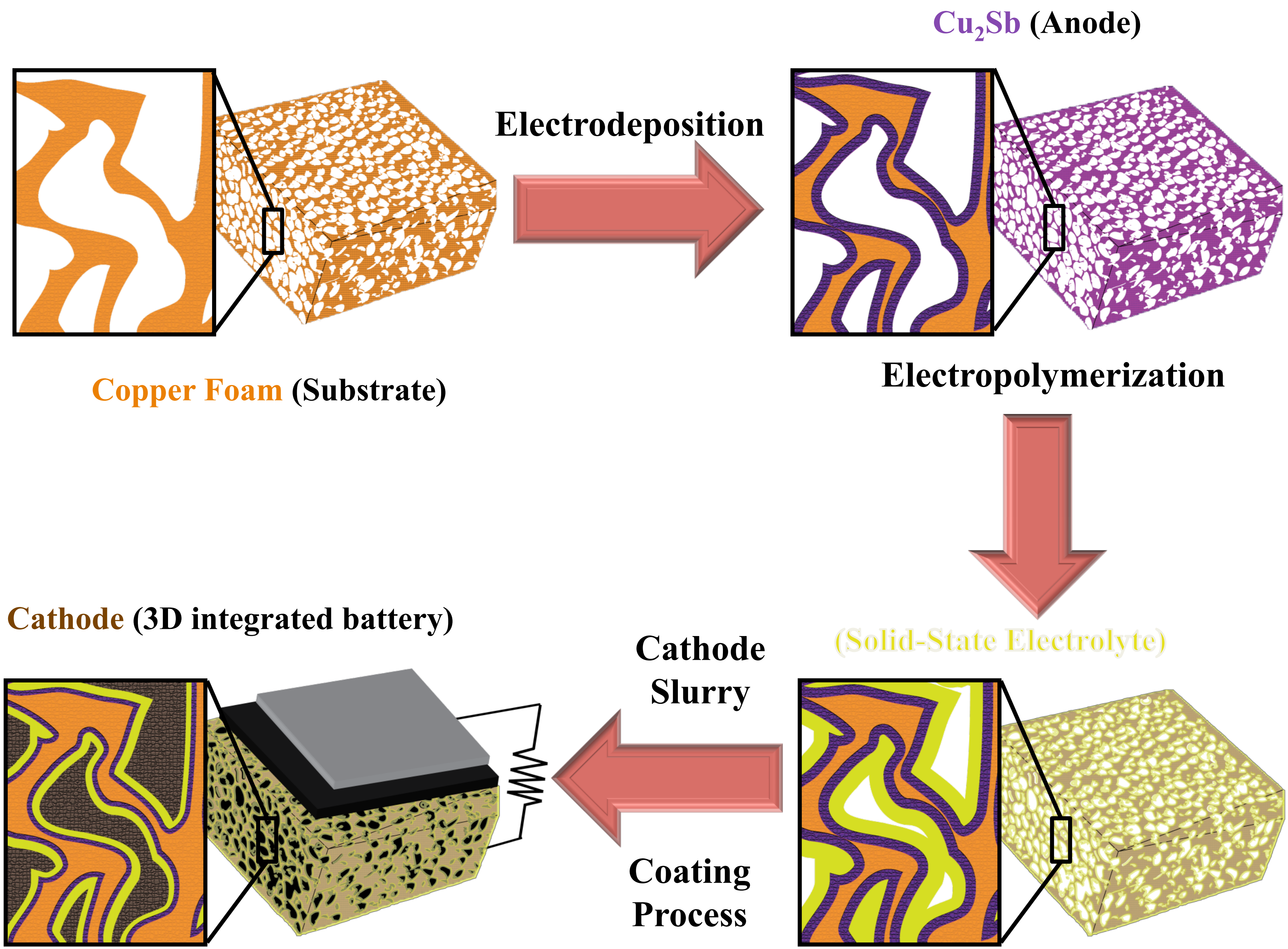
Three Dimensional Battery Architectures



Stein, A. *et al*. *Adv. Mater.* **2006**, *18*, 1750

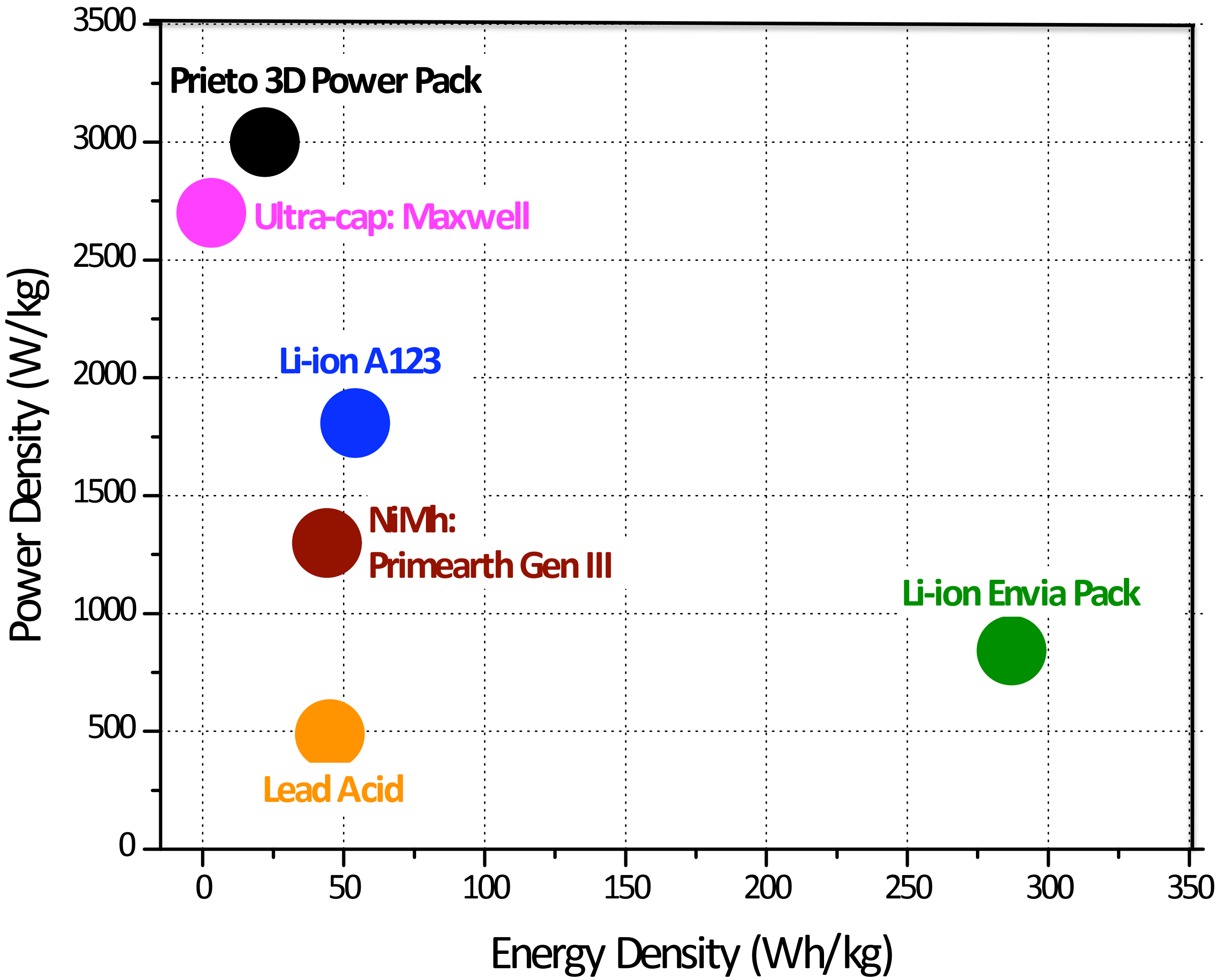


Long, J. and Rolison, D. *Acc. Chem. Res.,* **2007***, 40,* 854



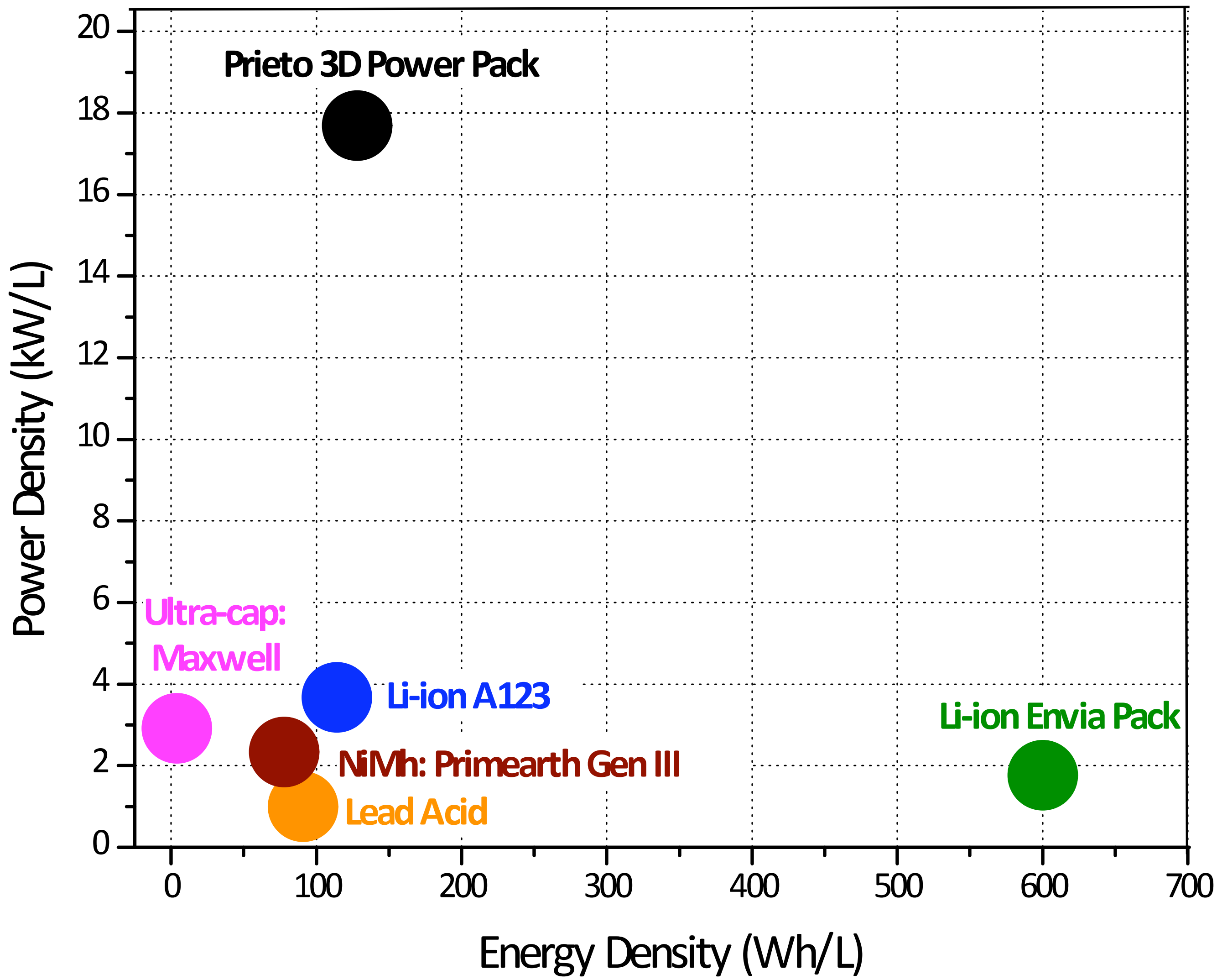
Electrodeposition
Cu2Sb (Anode)
Copper Foam (Substrate)
Electropolymerization
Cathode (3D integrated battery)
Cathode
Slurry
Coating
Process
(Solid-State Electrolyte)

Theoretical Performance for a 3D Foam Architecture



Gravimetric power density is competitive with ultracapacitors

Theoretical Performance for a 3D Foam Architecture



For applications where volume is the most important factor, the proposed 3D battery is an exciting option

The Goals of the Proposed 3D Battery

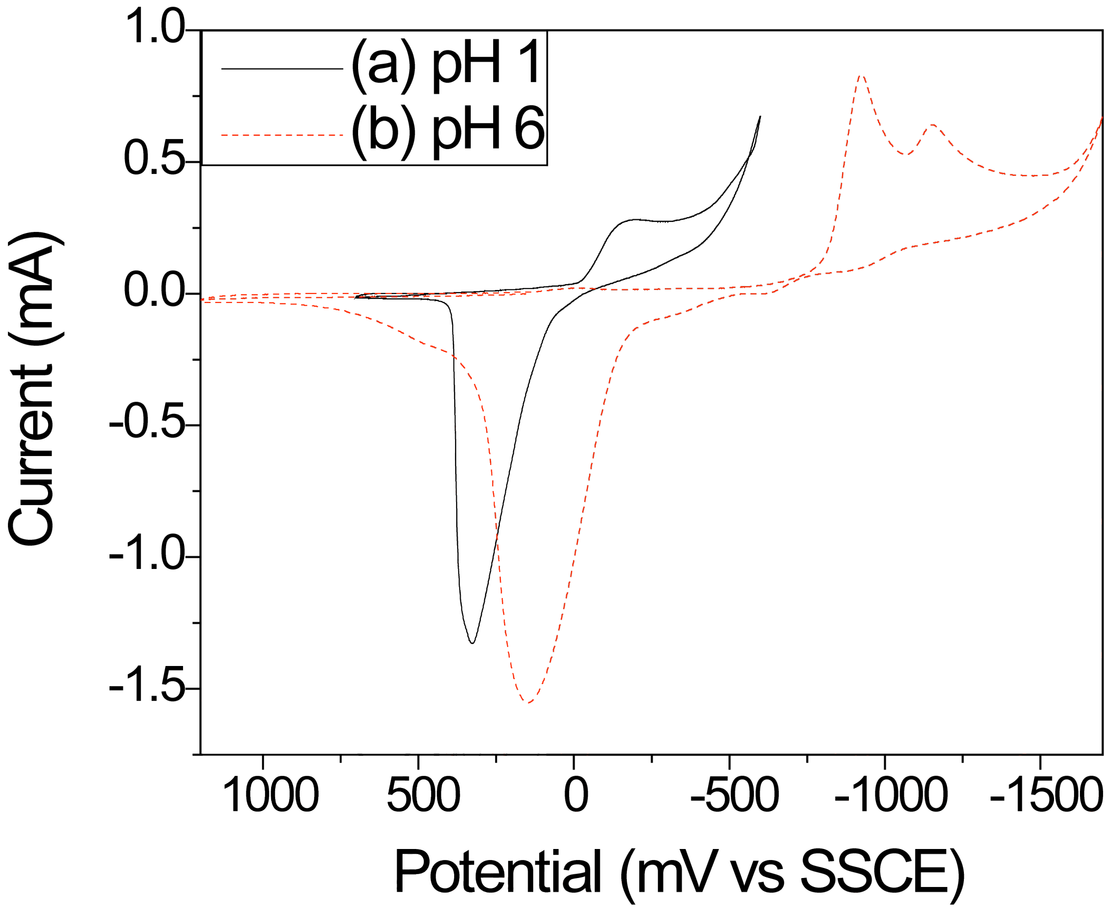
$$Power\ Density \propto \frac{Voltage \times Lithium\ ion\ conductivity \times Surface\ area}{Lithium\ ion\ transport\ length}$$

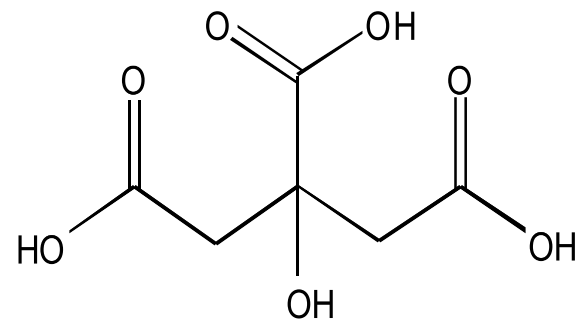
- **Battery Performance**
  - **Very high power density:** up to 1000x improvement
  - **Smaller battery size:** ≈ 2/3 the size for same energy density
  - **Long life:** Greater than 5000 cycles
  - **Safety:** No liquid electrolyte, no hydrofluoric acid production

- **Battery Manufacturing Process**
  - Traditional electroplating
  - Highly repeatable & scalable

- **Competitive Cost:**
  - Current projection is ≈ $348/kWh
  - Industry leaders are currently ≈ $500-1000/kWh

Increasing the Electrochemical Window





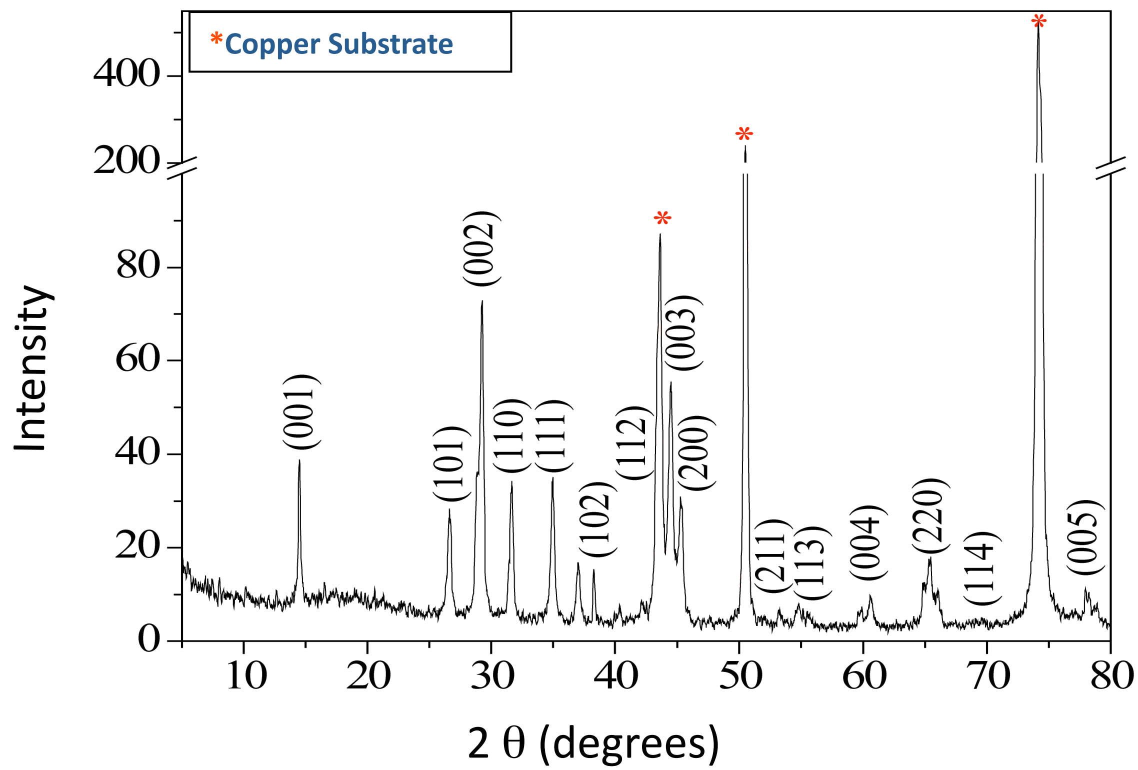
Solution conditions:
0.4 M citric acid
0.025 M Sb_2O_3
0.1 M $(Cu(NO_3)_2$
pH 6 (raised with KOH)

Working: Pt disk
Counter: Pt gauze
Reference: SCCE
Scan rate: 250 mV/s

$$2[Cu_2Cit_2H_{-1}]^{3-} + 2[SbCitH_{-1}]^{-} + 4H_3O^{+} + 14e^{-} \rightarrow 2Cu_2Sb + 6Cit^{3-} + 4H_2O$$

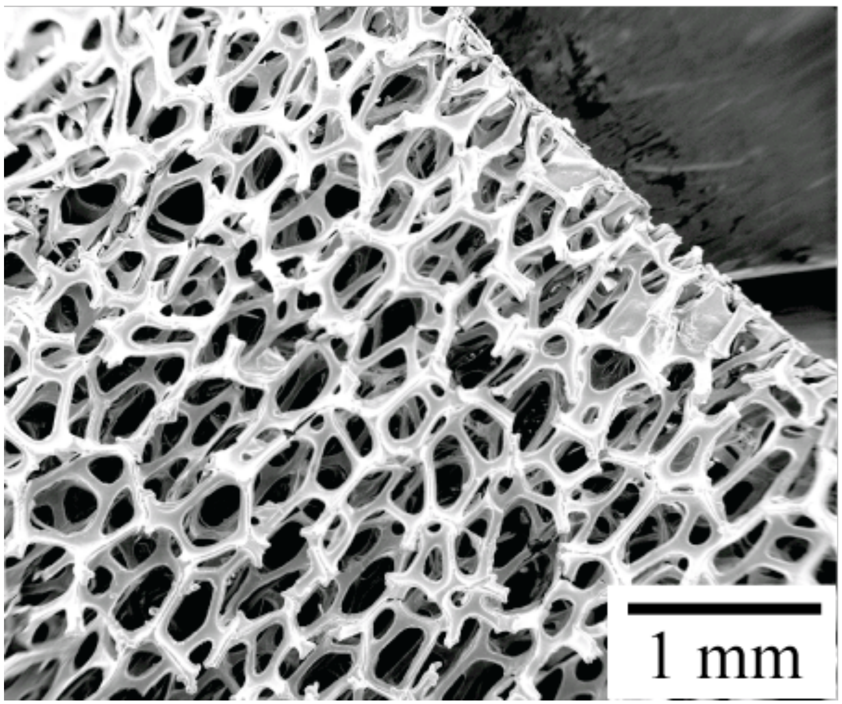
Mosby, J., Prieto A.L *J. Am. Chem. Soc.* **2008**, *130*, 10656

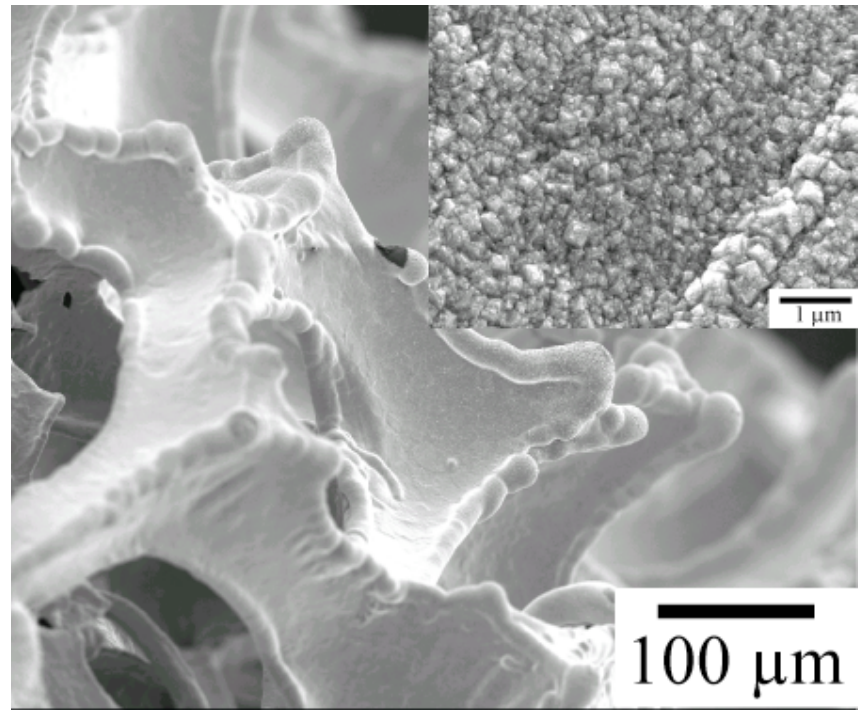
Direct Deposition of Crystalline Cu_2Sb



Direct deposition of crystalline, stoichiometric films from aqueous solution at room temperature

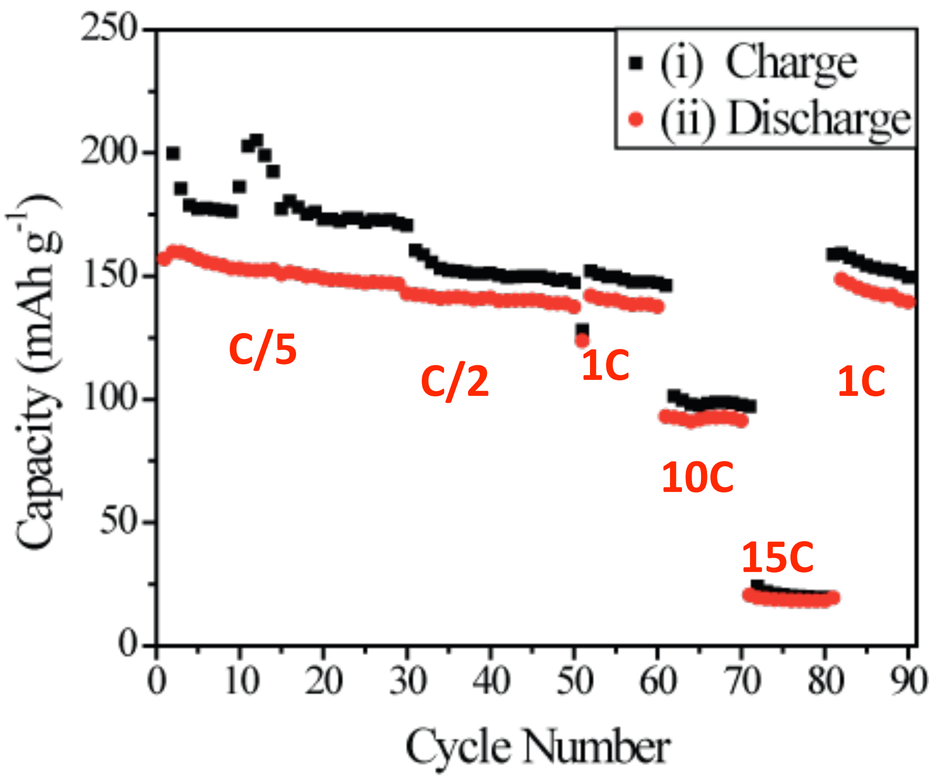
Conformal Deposition onto High Surface Area Structures





Short deposition times (2 minutes) result in a thin, conformal coating of Cu_2Sb on high surface area Cu foam.

Cycling Performance of Thin Cu_2Sb



- Exhibits same charge and discharge plateaus as thin film Cu_2Sb
- Great rate performance
  - 100 mAh g^{-1} at 10C (1mA cm^{-2})
  - Only 1% capacity loss at 1C
- No binders necessary

"Long" Term Cycling Studies

Anode: Cu_2Sb on Cu foam

Separator: Commercial

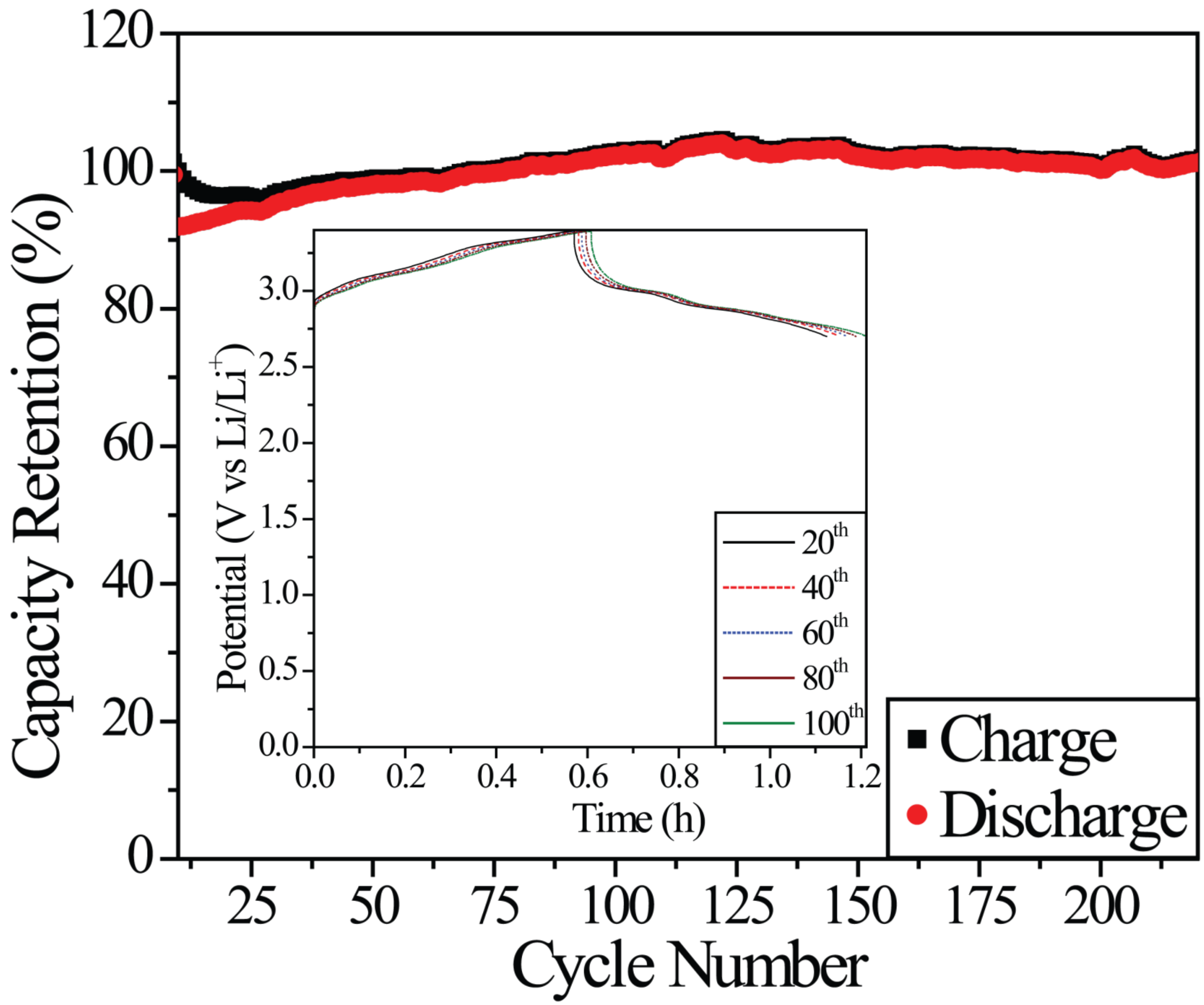
Electrolyte: 3:7 (by volume) EC:DEC with 1M $LiPF_6$

Cathode: $LiCoO_2$, Graphite, and PVDF

Rate: Between 1-2 C

Note: The formation procedure is completed during the first ten cycles and have been removed for clarity

Excellent capacity retention at 220 cycles



"Long" Term Cycling Studies

Anode: Cu_2Sb on Cu foam

Separator: Commercial

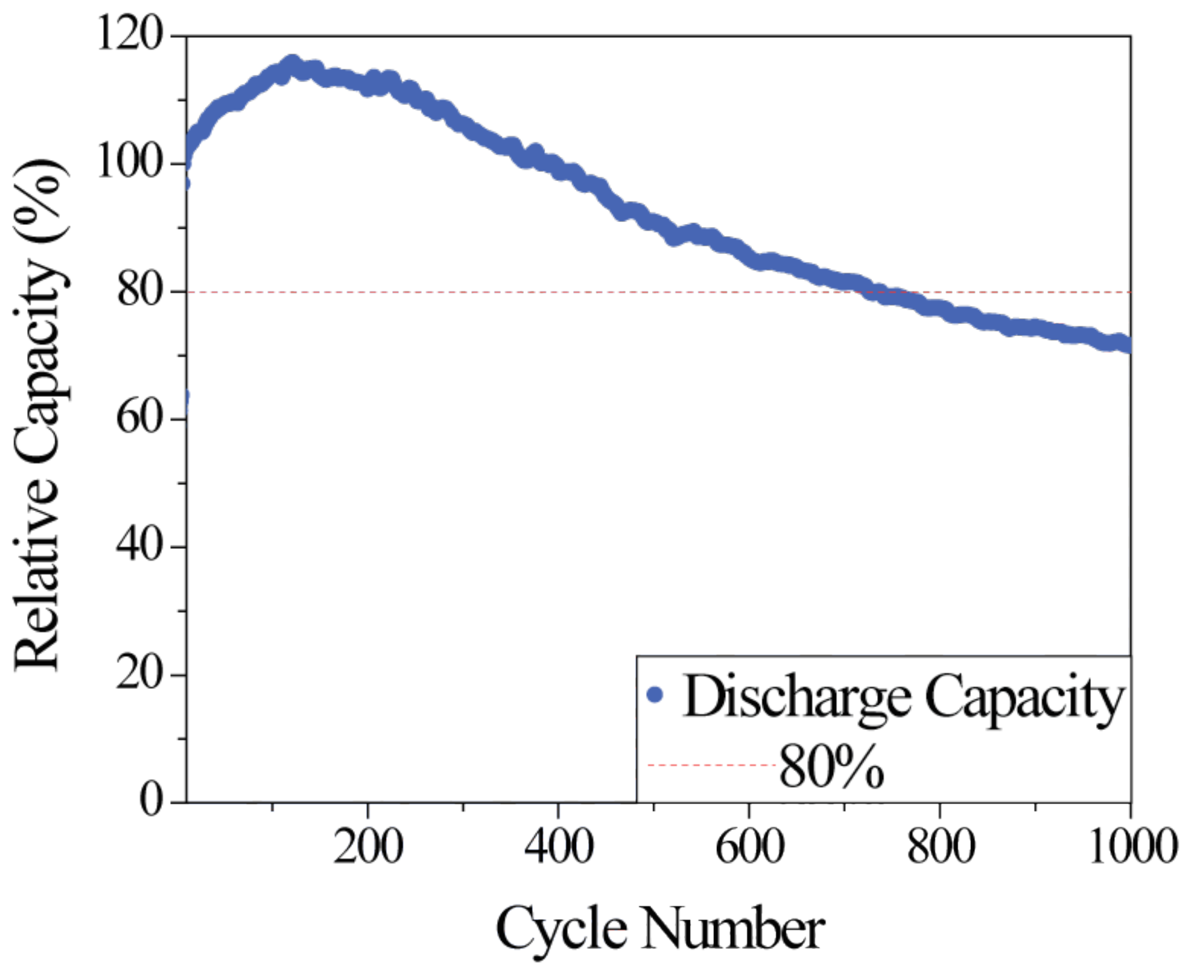
Electrolyte: 3:7 (by volume) EC:DEC with 1M $LiPF_6$

Cathode: $LiCoO_2$, Graphite, and PVDF

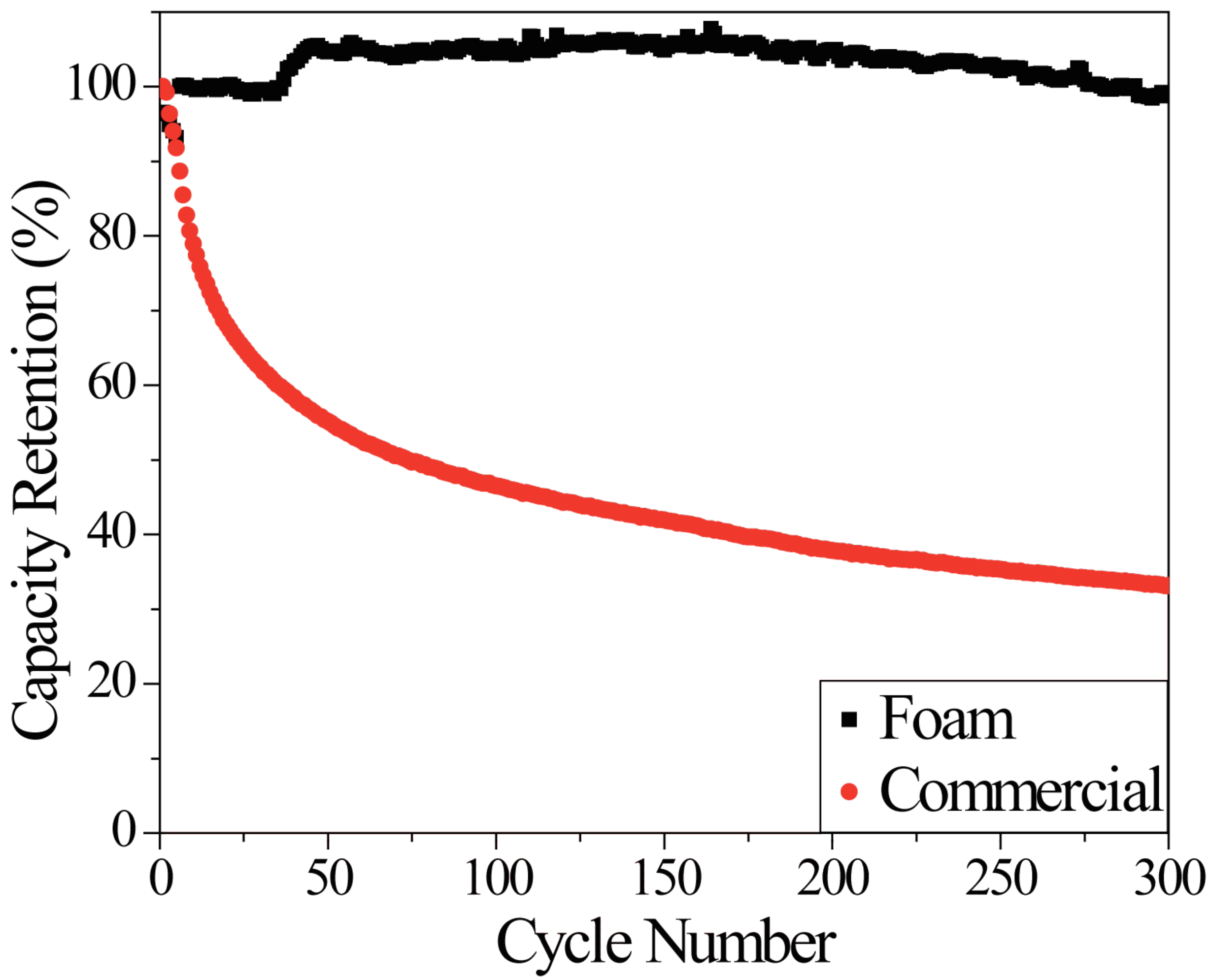
Rate: Between 1-2 C

Note: The formation procedure is completed during the first ten cycles and have been removed for clarity

Excellent capacity retention at 725 cycles

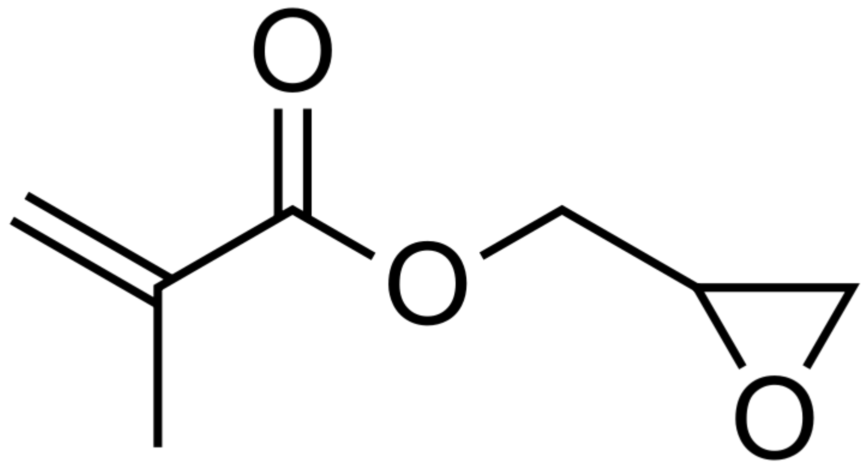


Foam 5-stack versus Commercial Batteries



High surface area anode exhibits significantly enhanced cycle life versus commercially available graphite anodes at 2C charge and discharge rates

Electrolyte: Glycidal Methacrylate



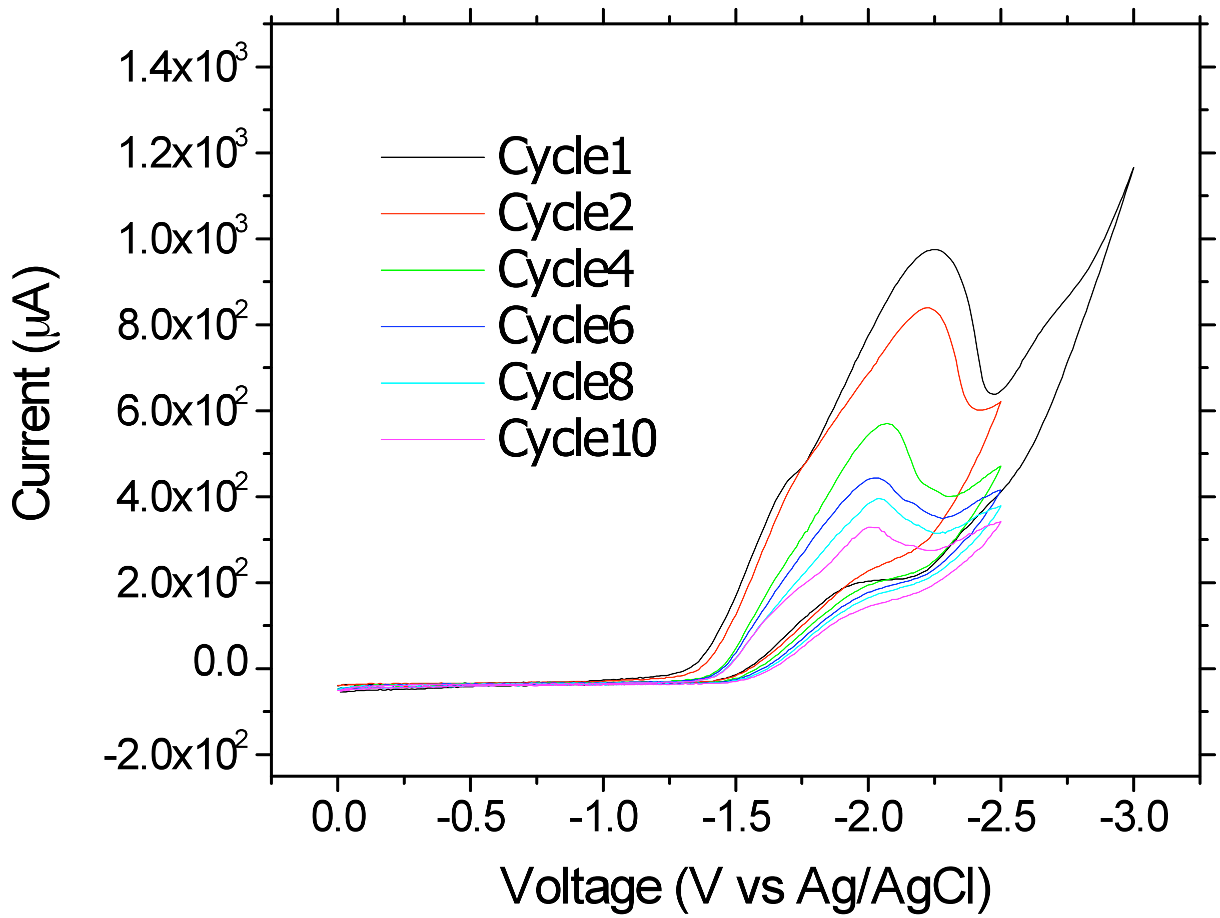
Reductive radical polymerization

Analogous to PEO (industry standard)

Self-limiting polymerization

Amenable to salt doping

Potentiocycling Polymerization



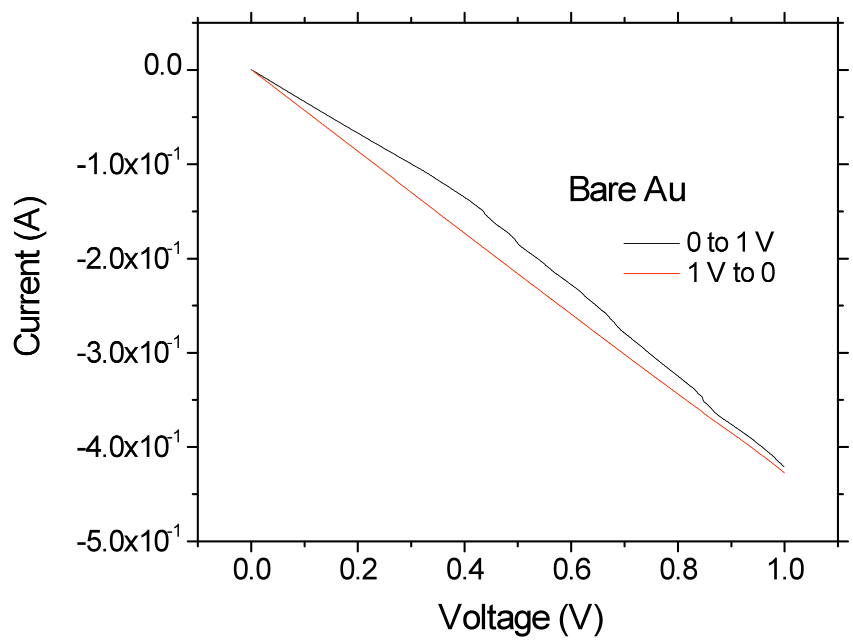
Solvent: DMF
[GYM] = 2 M
[$TBAClO_4$] = 0.5 M

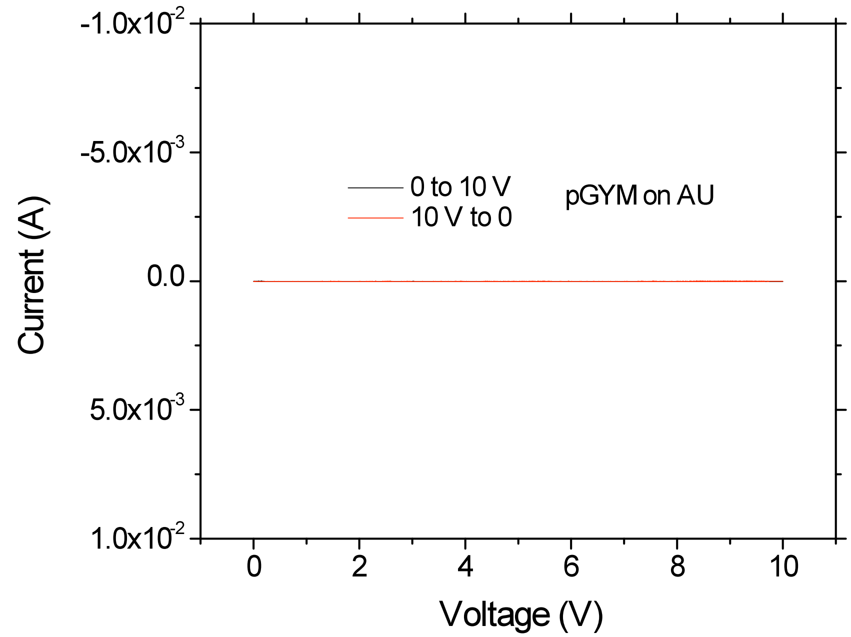
C: Pt mesh
R: Ag/AgCl (LiCl)
W: Au on glass

v = 0.1 V/s
10 cycles

Current decreases with increasing cycles, consistent with self-limiting behavior

Linear Sweep Voltammetry: Thin Film Studies





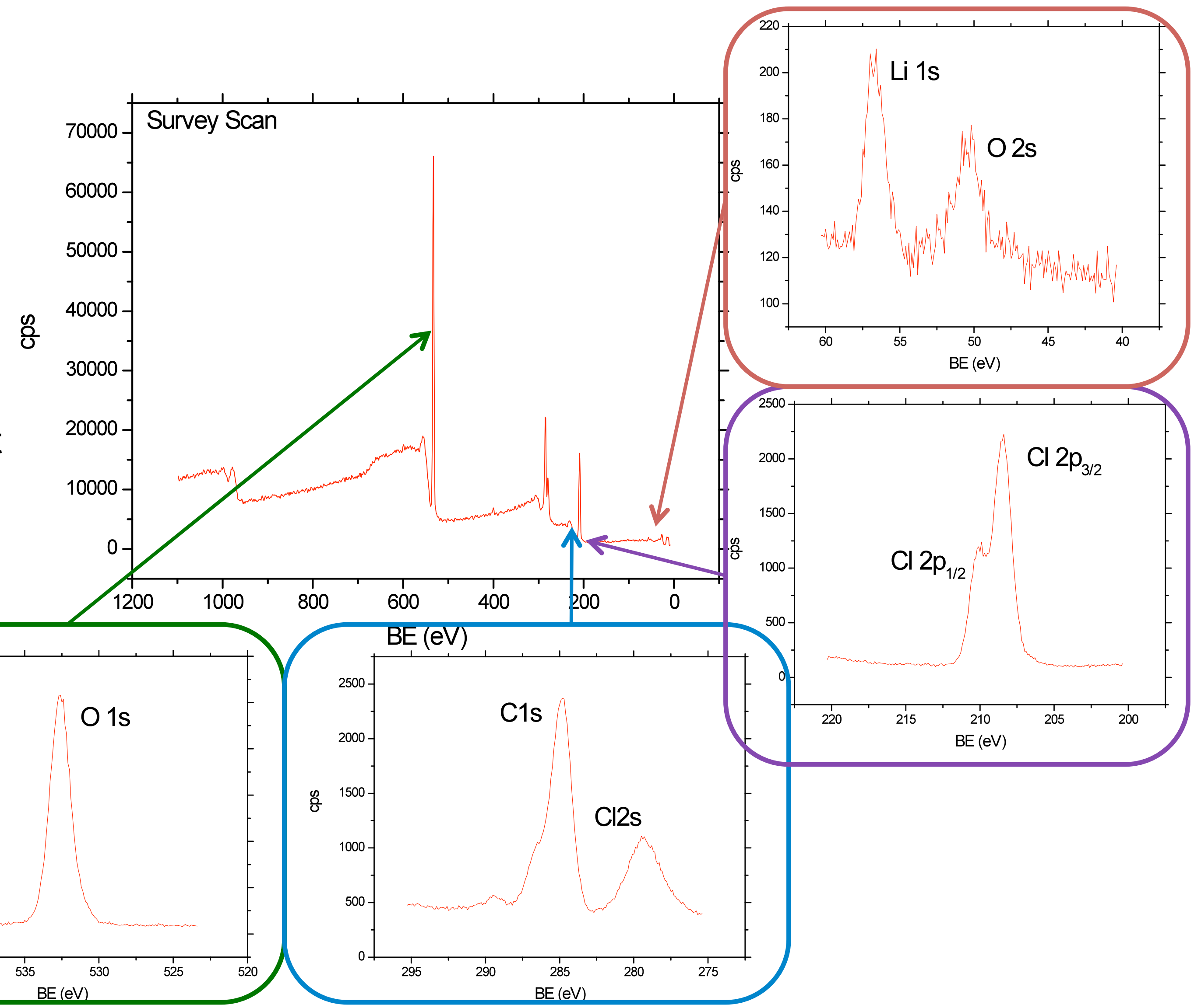
Polymer modified Au is electrically insulating…

Next step is determining film thickness

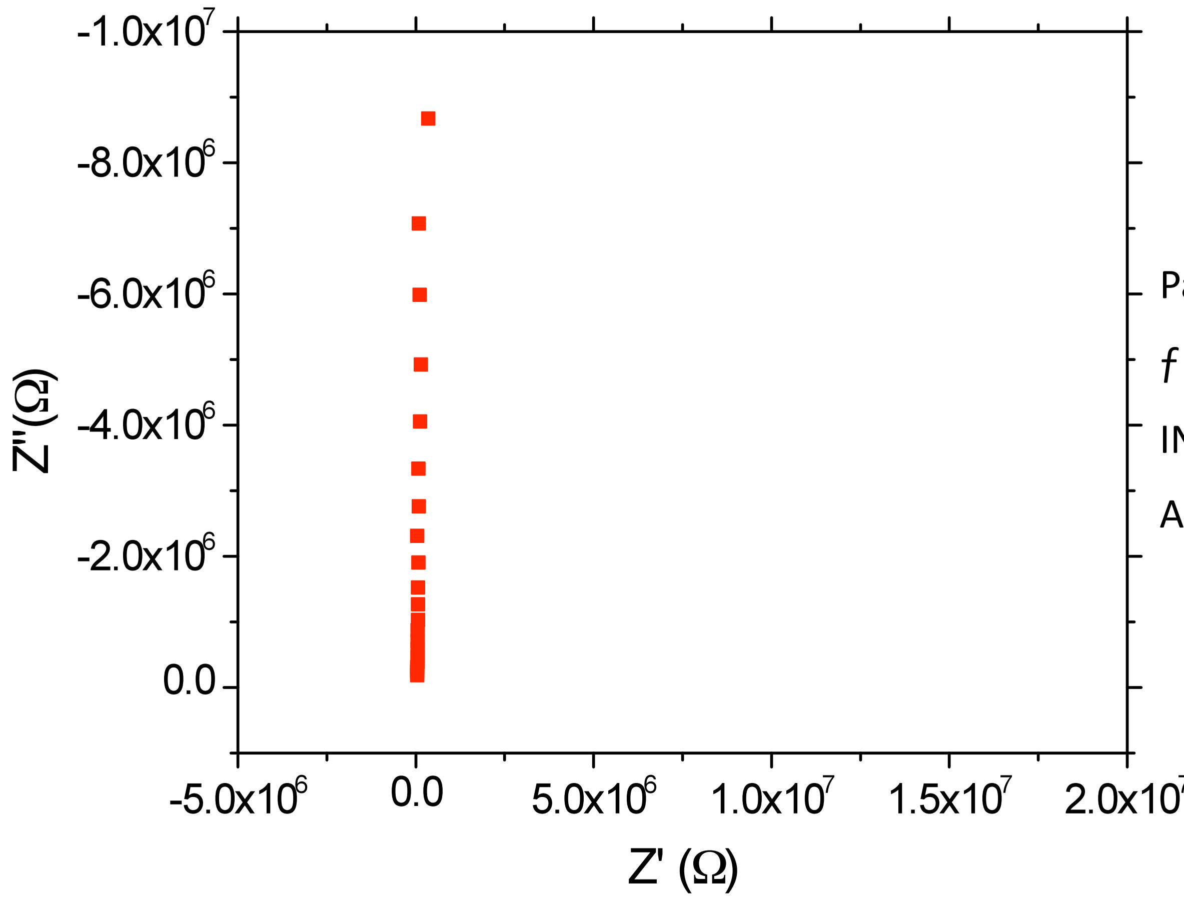
GYA: Doping with $LiClO_4$ in PC

Doping Method:

- Placed in 1 M $LiClO_4$ / PC for 24 h
- Dipped in clean PC
- Dried *under vacuum* at 65 ^{o}C for 24 h



Solid State Impedance Spectroscopy: pGYM on Au



Parameters:

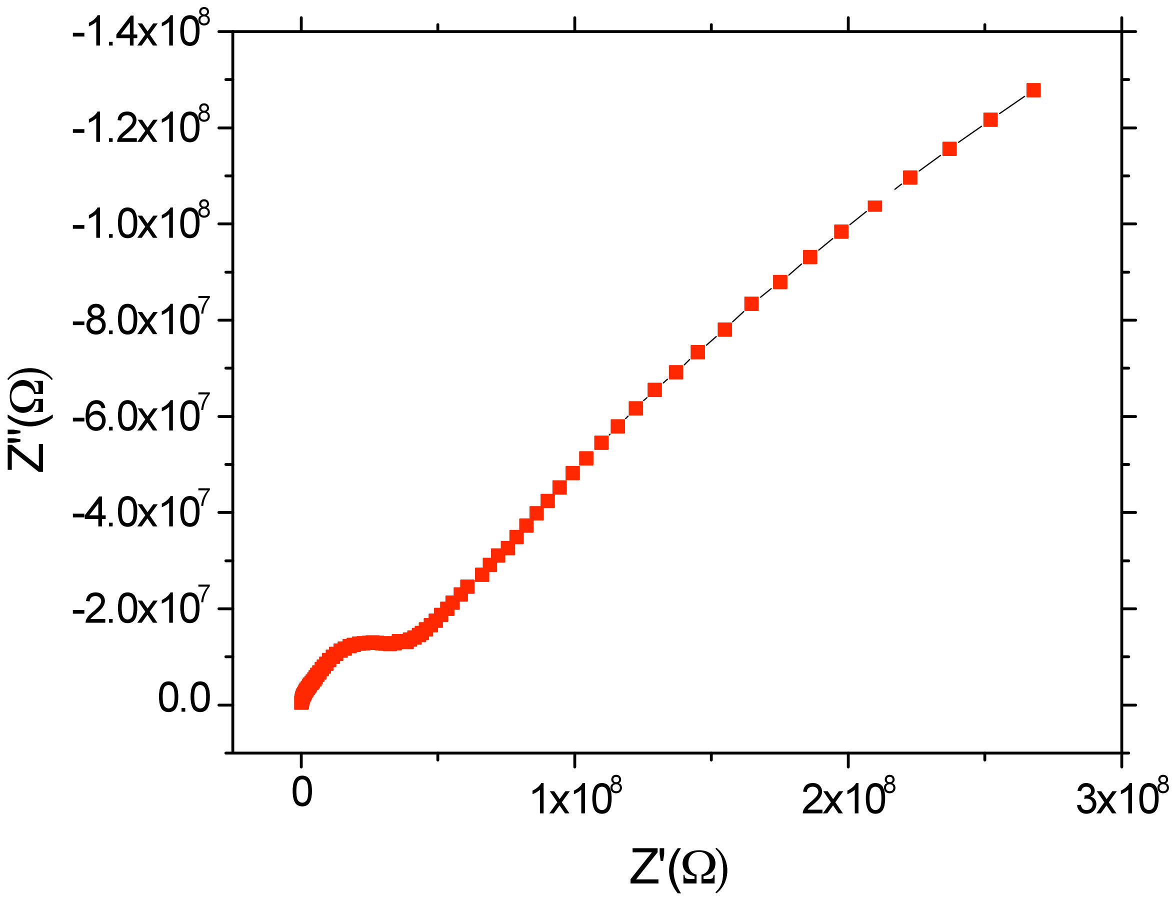
f = 1 x 10^5 – 1 x 10^{-2} Hz

INI E = 0 V

A.C Amp. = 0.005 V

Undoped polymer films are good dielectrics

Solid State Impedance Spectroscopy: pGYM:$LiClO_4$ on Au



Parameters:

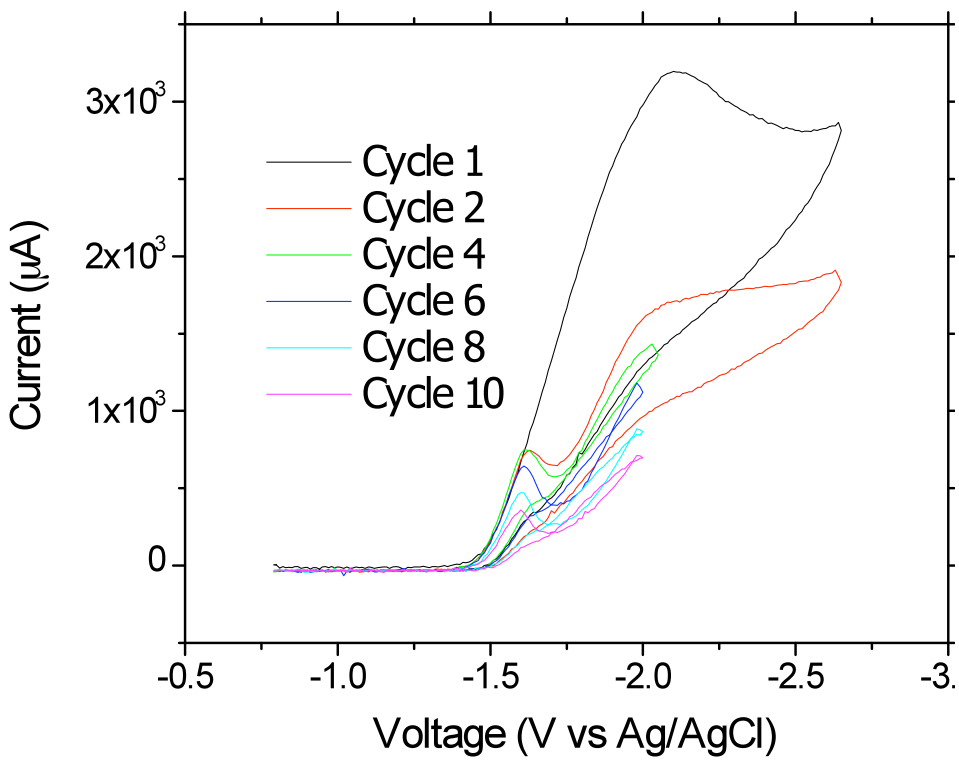
f = 1 x 10^5 – 1 x 10^{-2} Hz

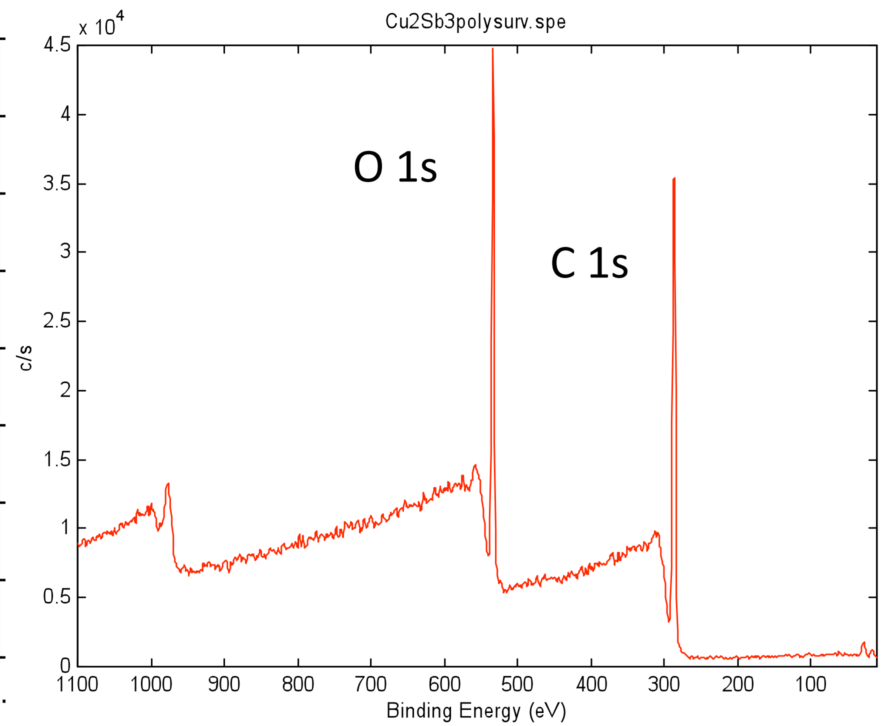
INI E = 0 V

A.C Amp. = 0.005 V

Doped polymer films are ionically conductive

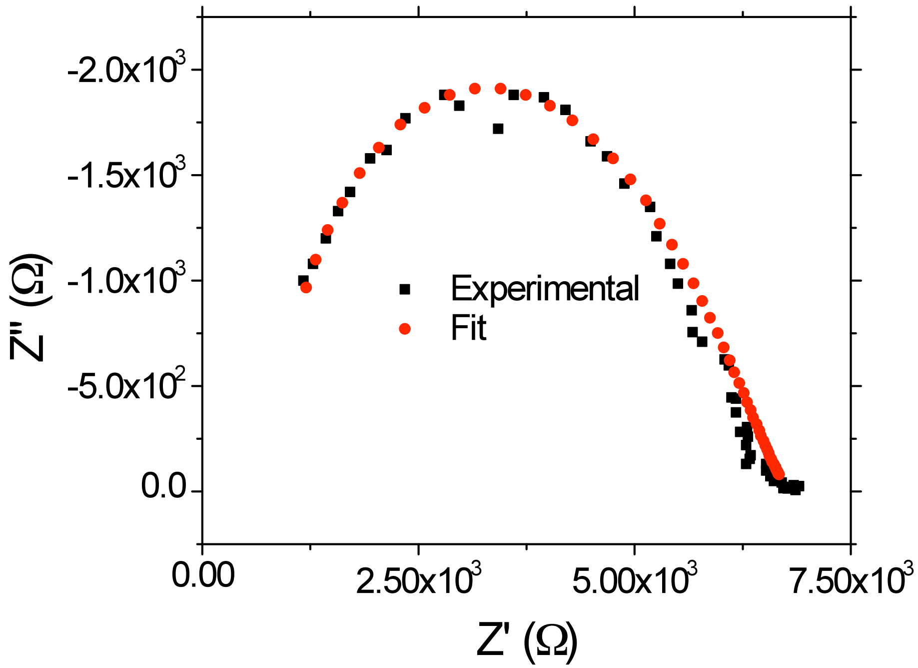
Integrating the Anode and Polymer Electrolyte

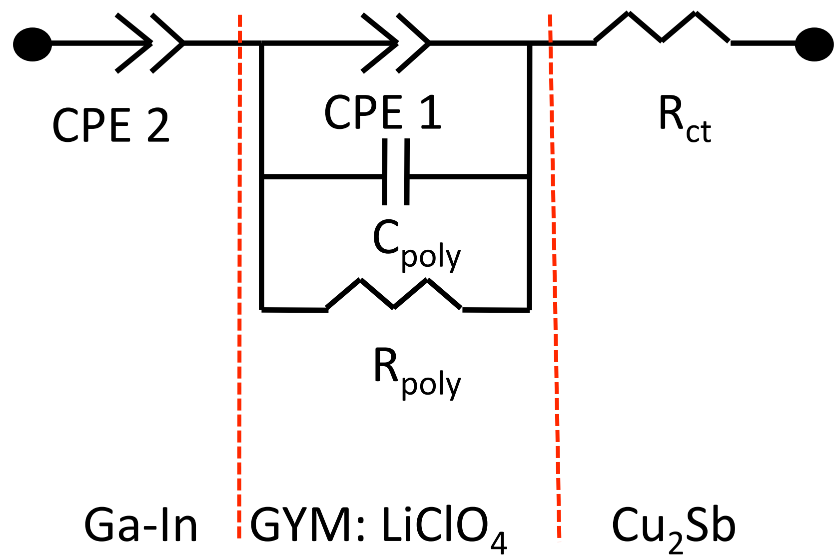




Good coverage on Cu_2Sb films

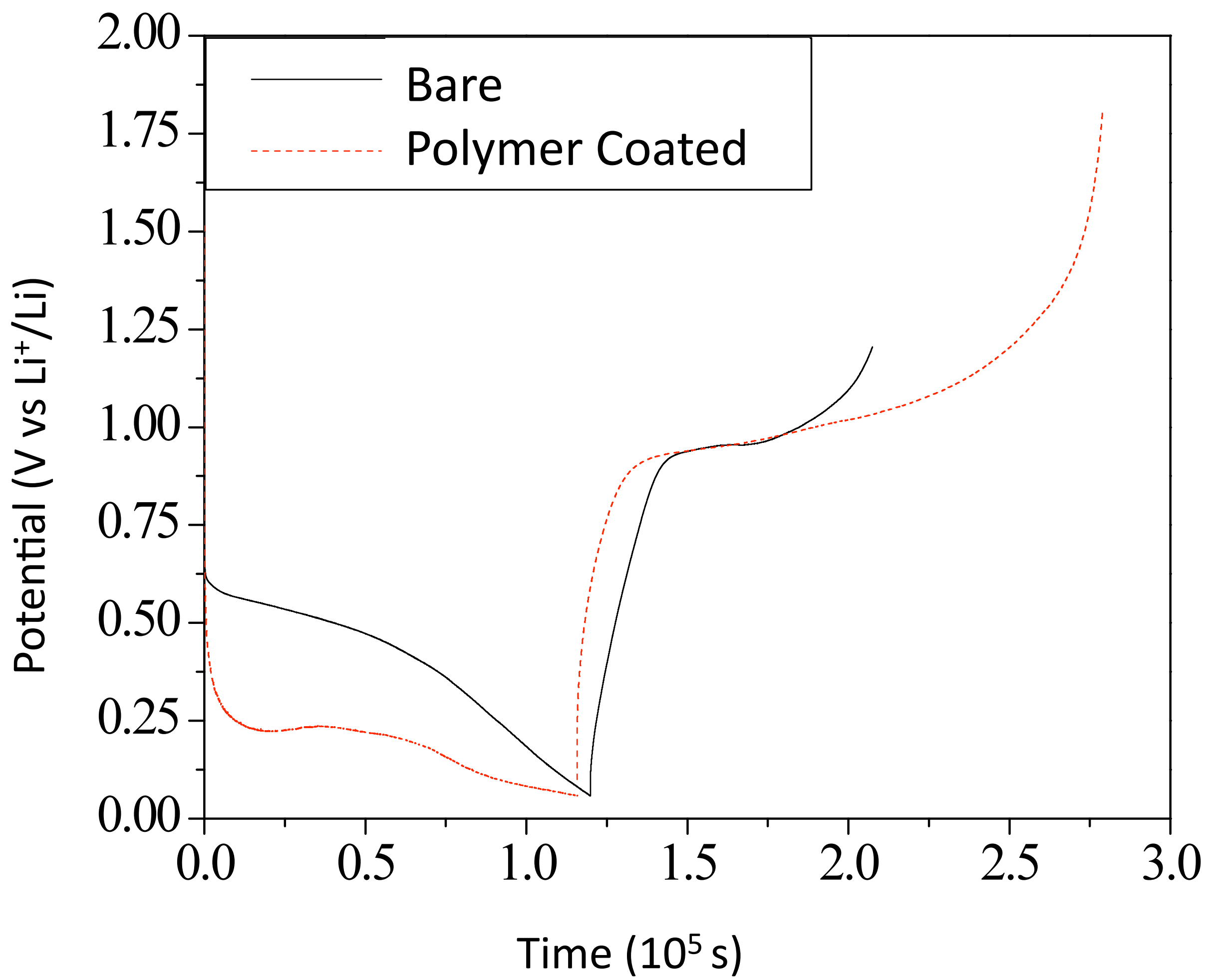
GYM on Cu_2Sb





Doped polymer films on Cu_2Sb are ionically conductive

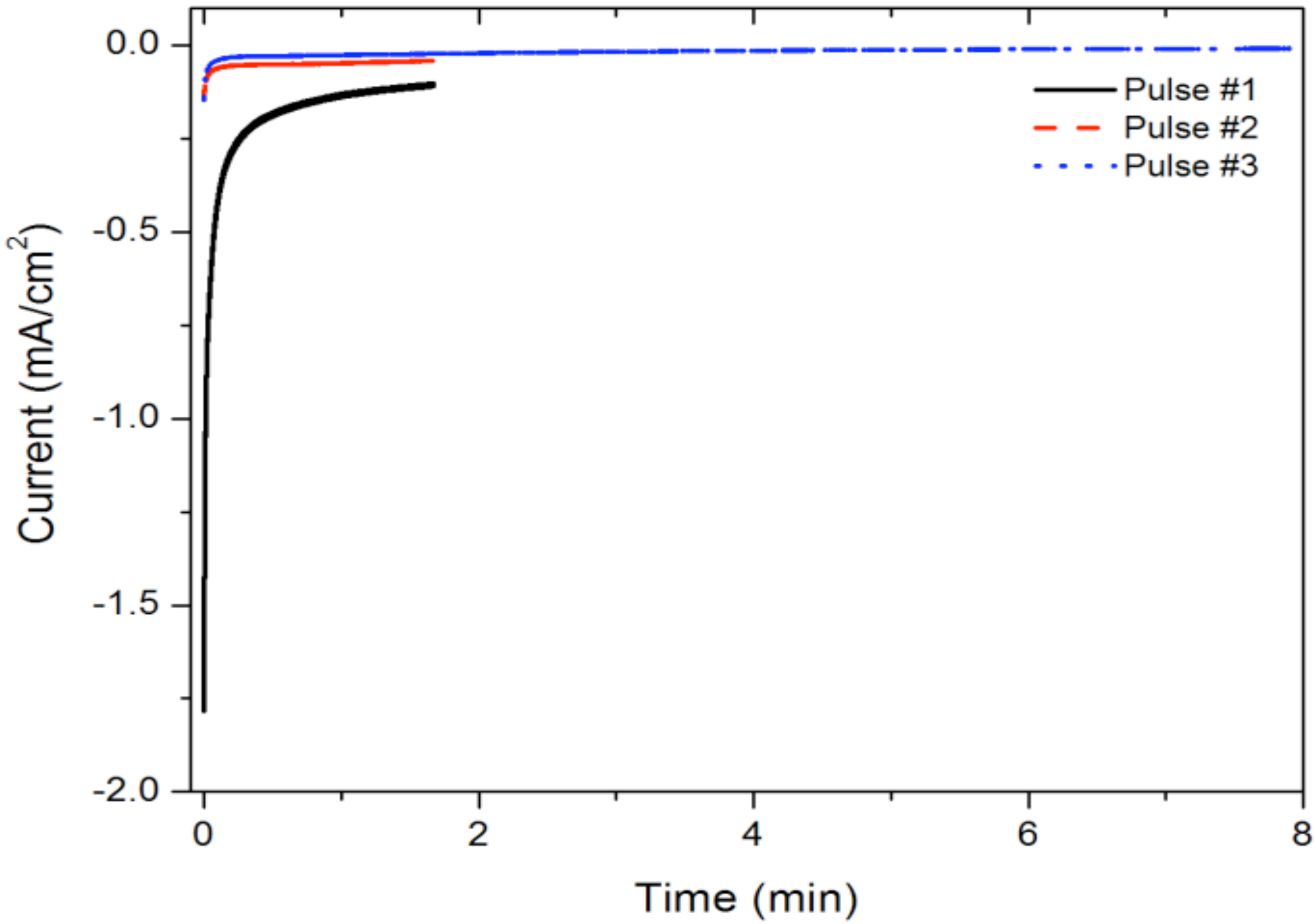
GYA on Cu_2Sb



Ethylene carbonate
Diethylene carbonate (1:1)
1 M $LiPF_6$
Working: Cu_2Sb /Cu
Counter: Li foil
Reference: Li foil
Scan rate: C/4

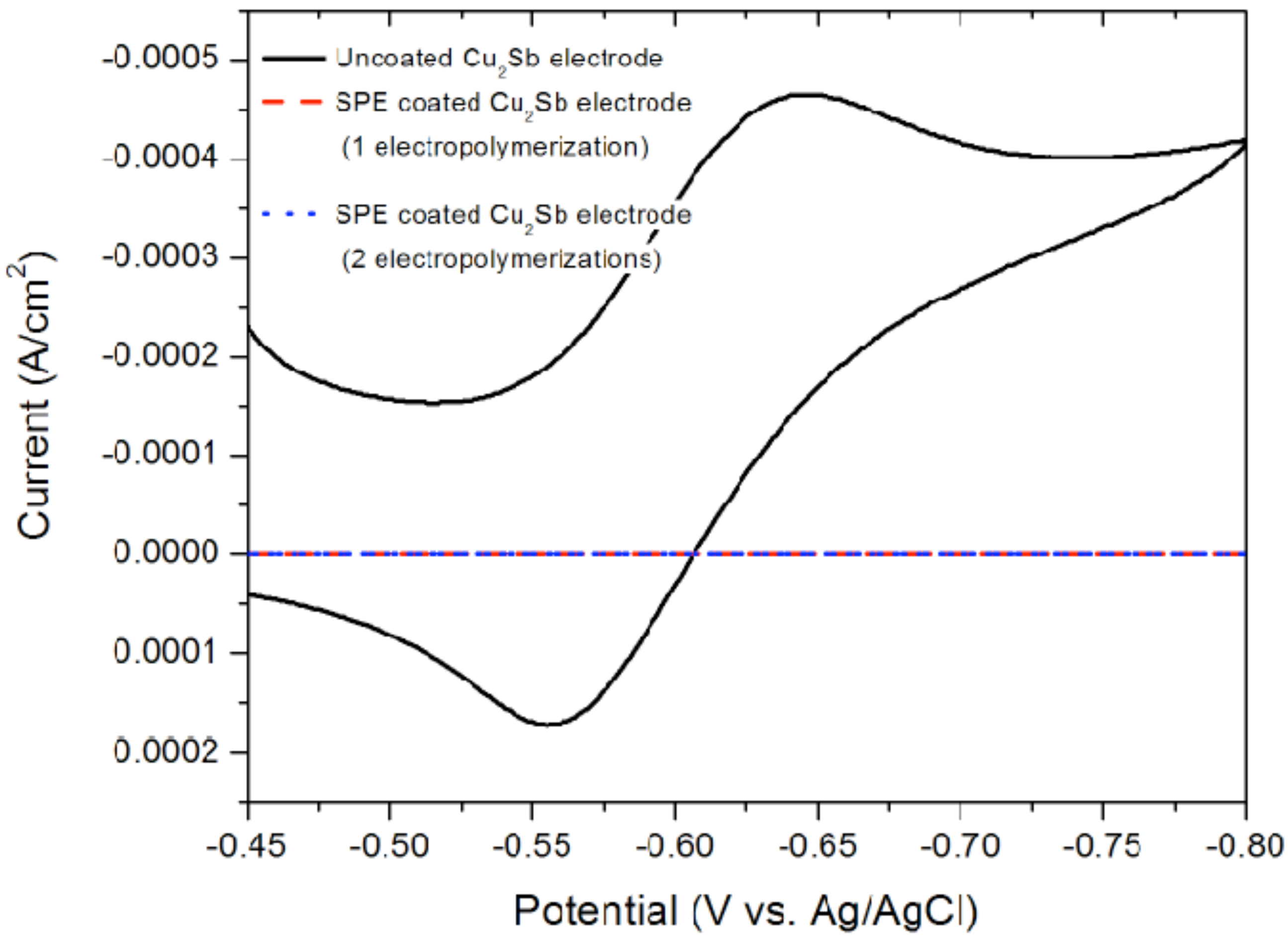
Cu_2Sb / GYM: $LiClO_4$ successfully cycles

Optimized Electrochemical Polymerizations



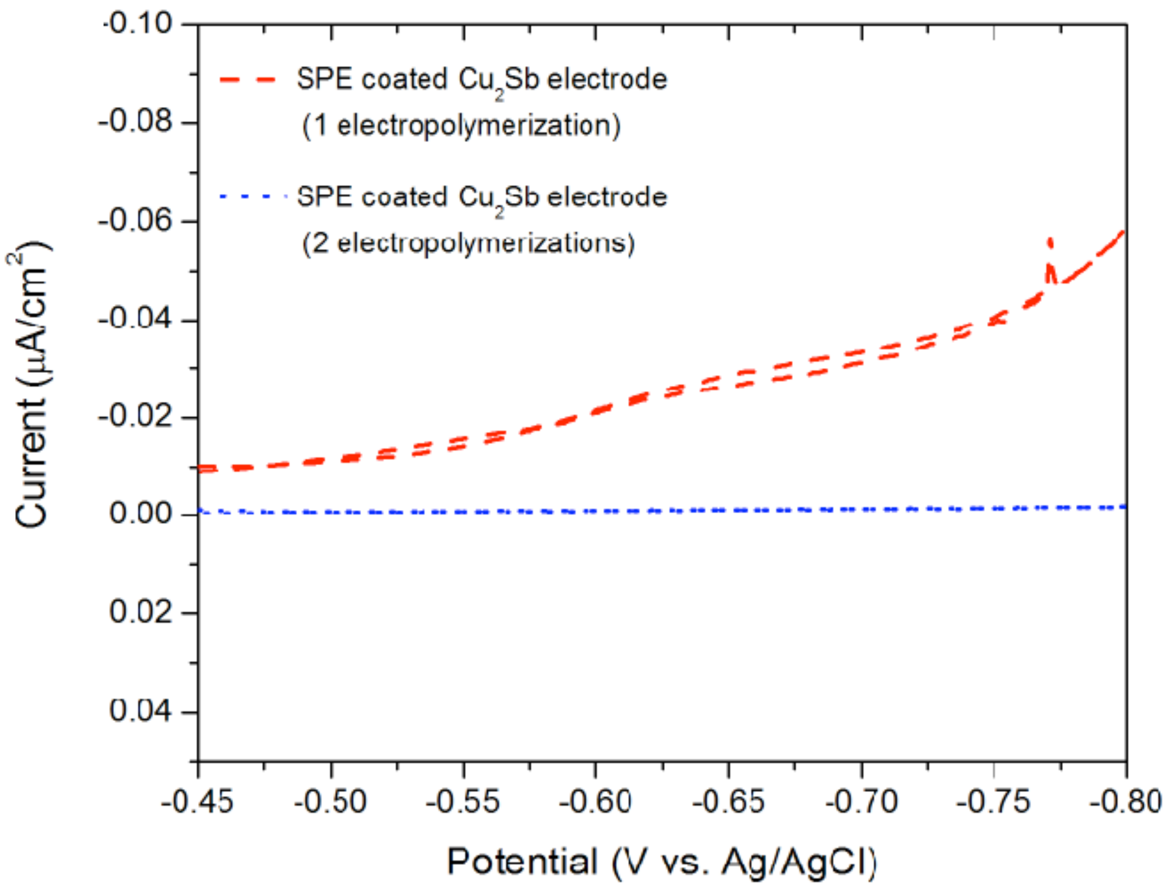
Polymer electrolytes have to be electrically insulating, but ionically conductive

Quick Ways to Test Quality



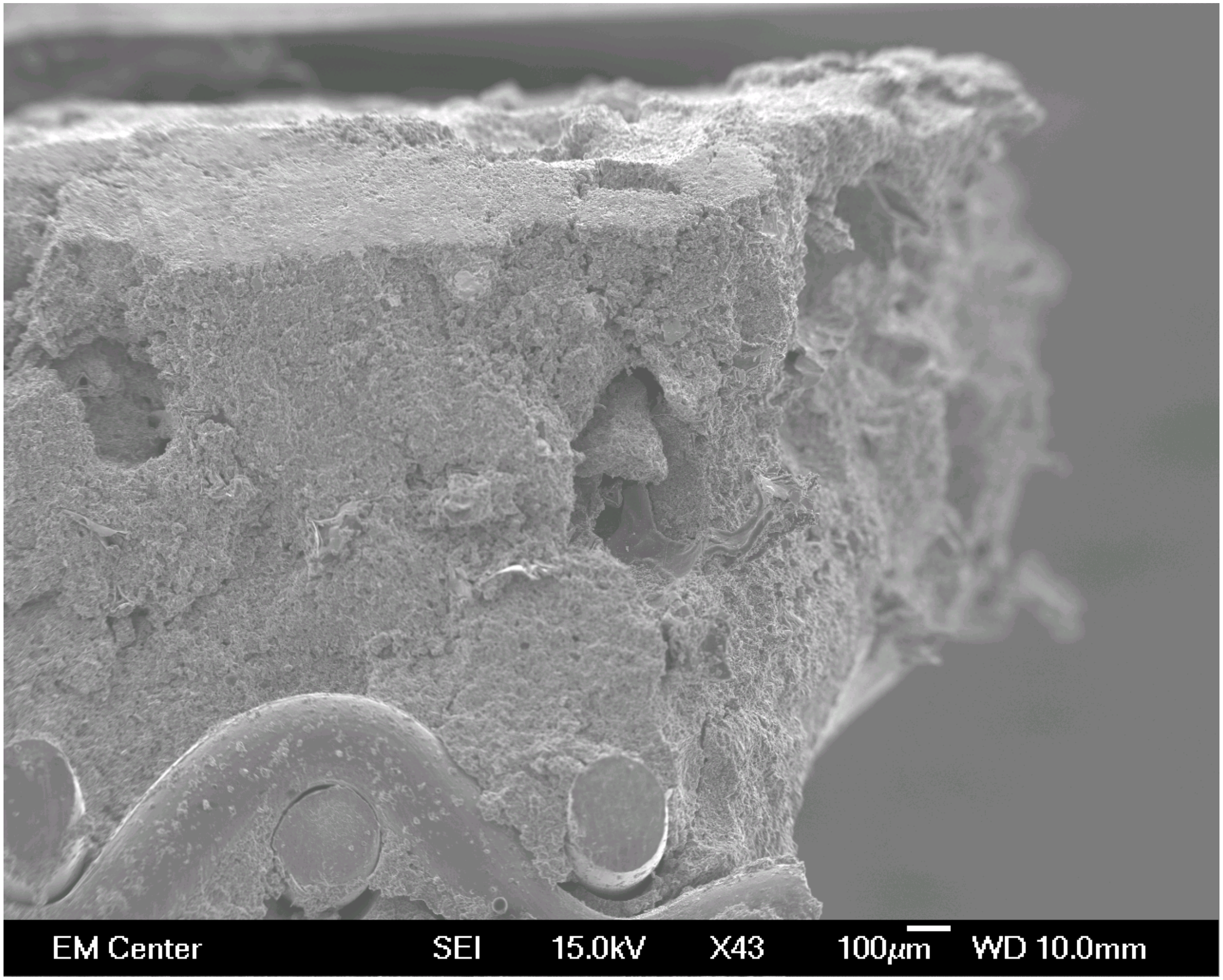
Redox shutoff experiments can detect defects the size of small molecules, which enable us to: 1) know the defect is there and 2) fill it in

Quick Ways to Test Quality

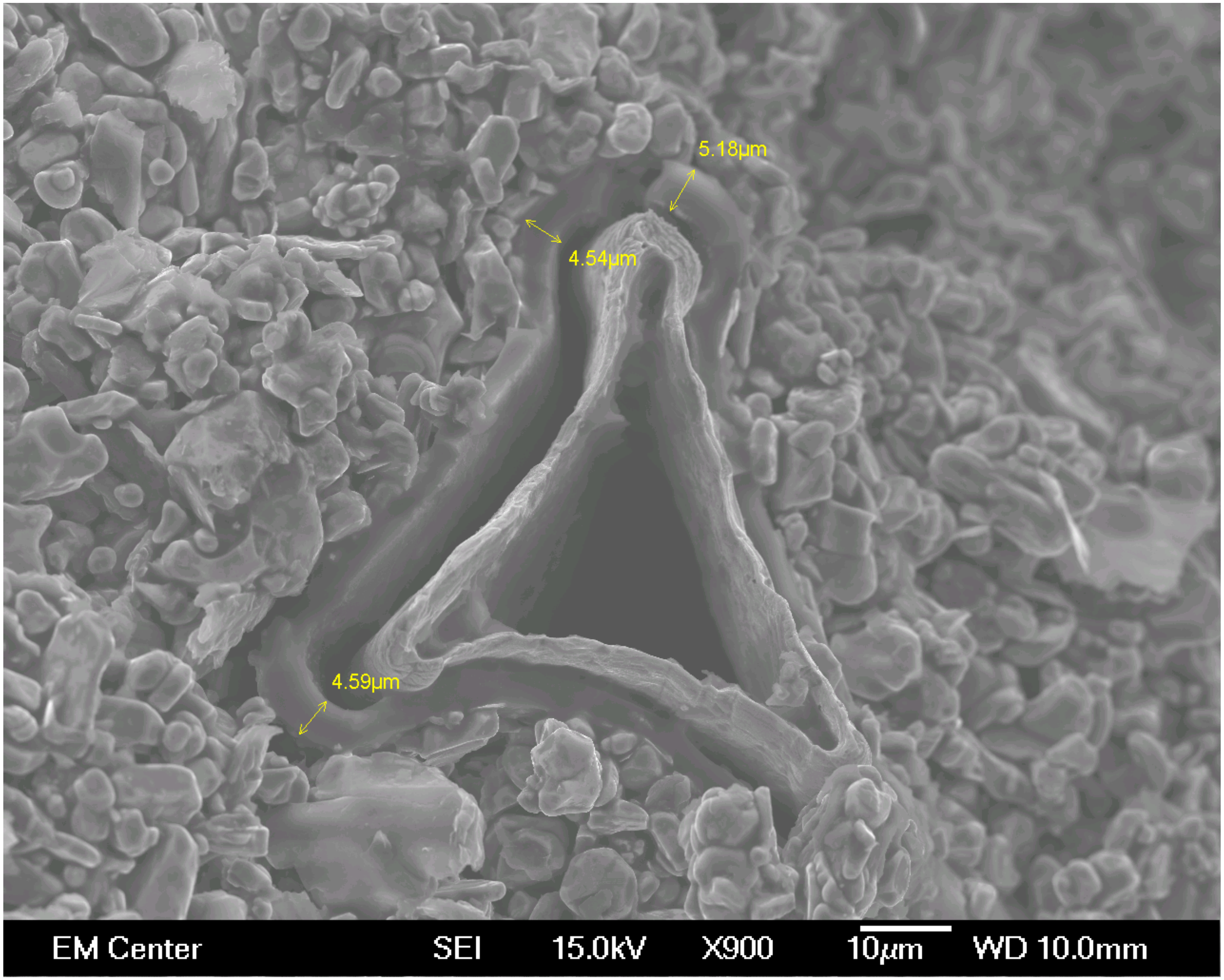


Redox shutoff experiments can detect defects the size of small molecules, which enable us to: 1) know the defect is there and 2) fill it in

Near Ideal Slurry Chemistry



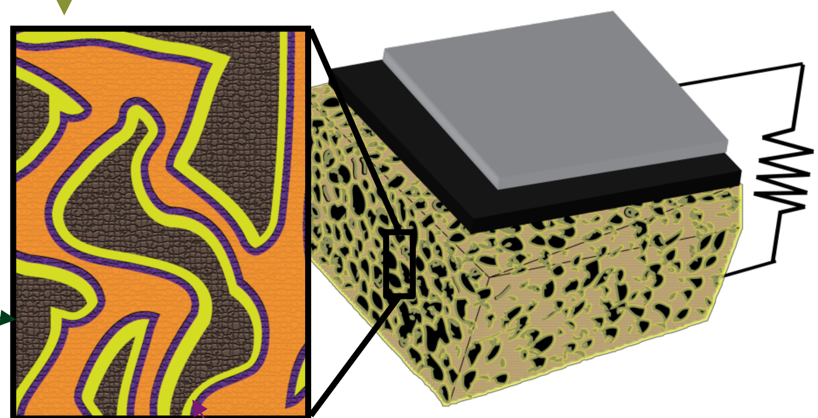
Good wetting of slurry to electrolyte



Future Work

Electrolyte:

A library of monomers have been electropolymerized, newest candidates show good ionic conductivity



Cathode

We have drop-casted particles of common cathode materials suspended in binder into our architecture.

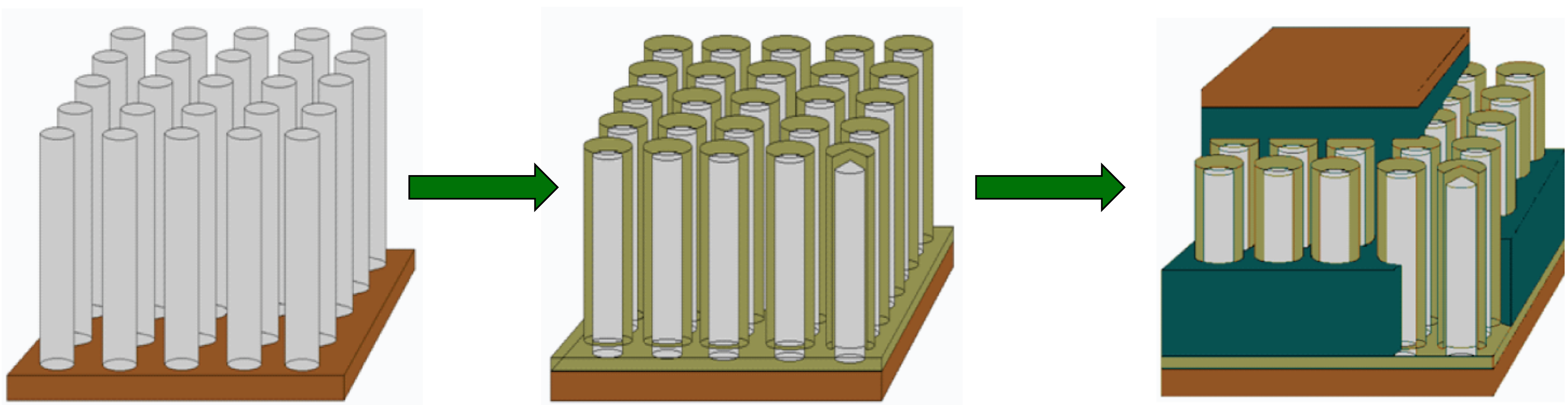
Anode:

Cu_2Sb has been electrodeposited with good crystallinity and conformal coverage

Proposed Architecture

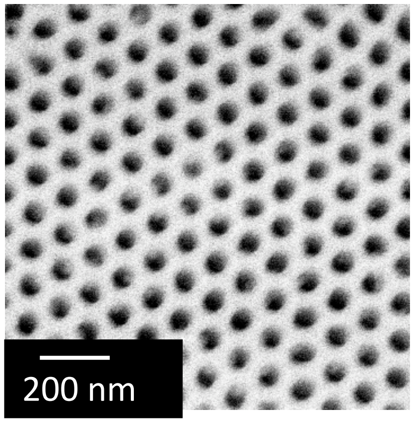
- High surface area — $1.2 \times 10^5\ cm^2\ g^{-1}$
- Small foot print
- Short lithium ion diffusion — 50 nm

→ High Power

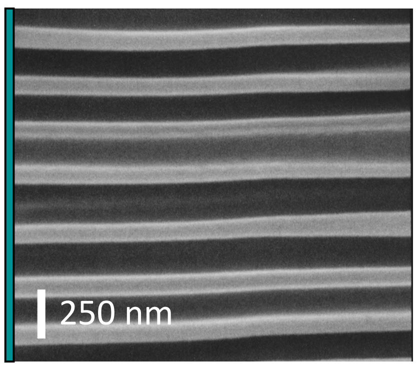


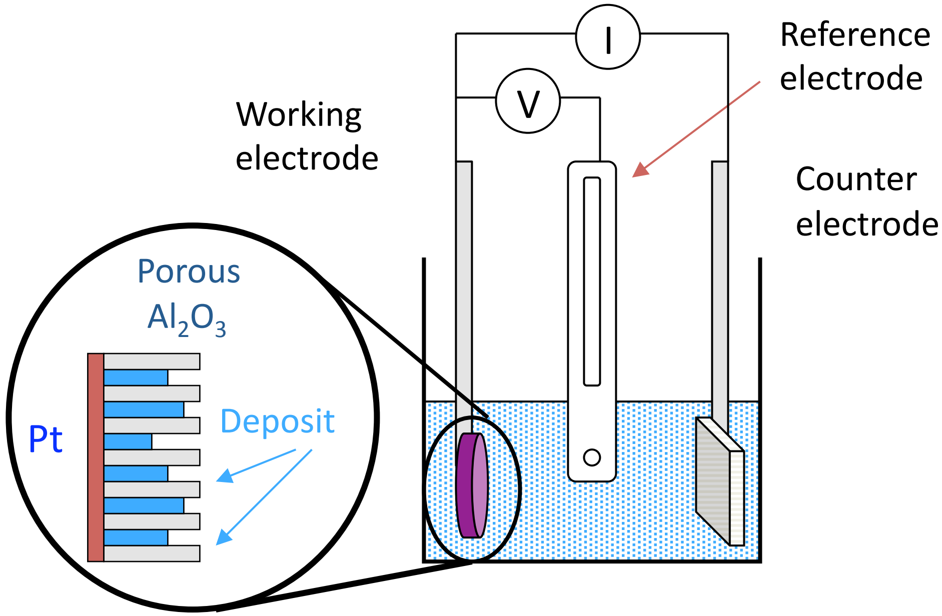
Anode	**Electrolyte**	**Cathode**
Electrodeposit anode material in AAO	Electropolymerize/ self assemble solid electrolyte	Solution synthesis of nanoparticles of cathode materials

Porous Anodic Alumina Templates



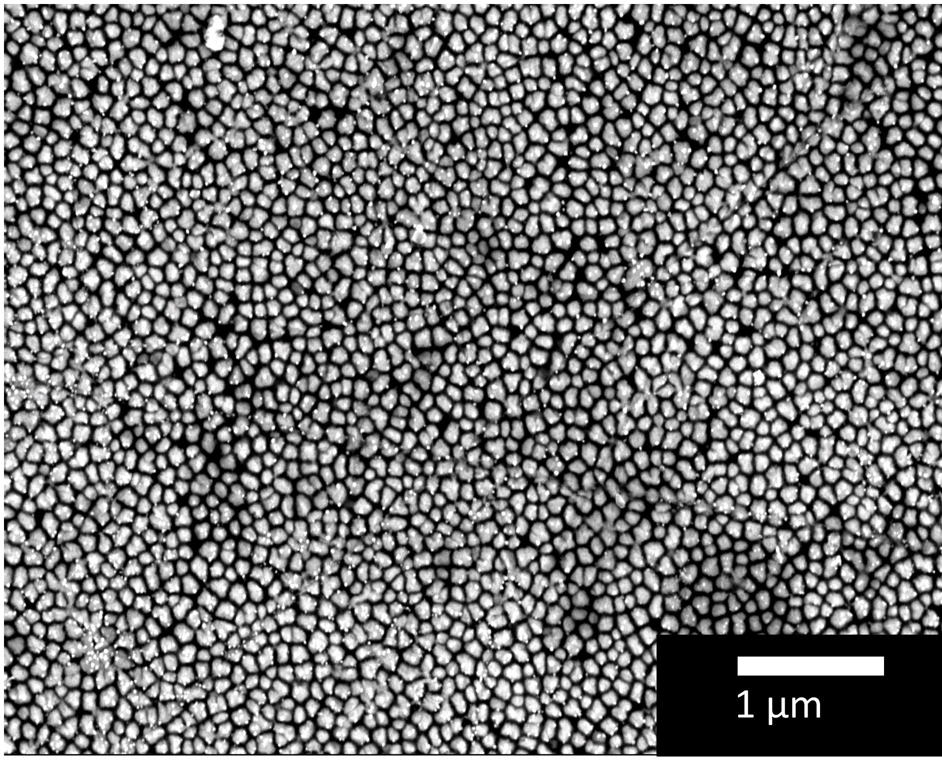
Pt

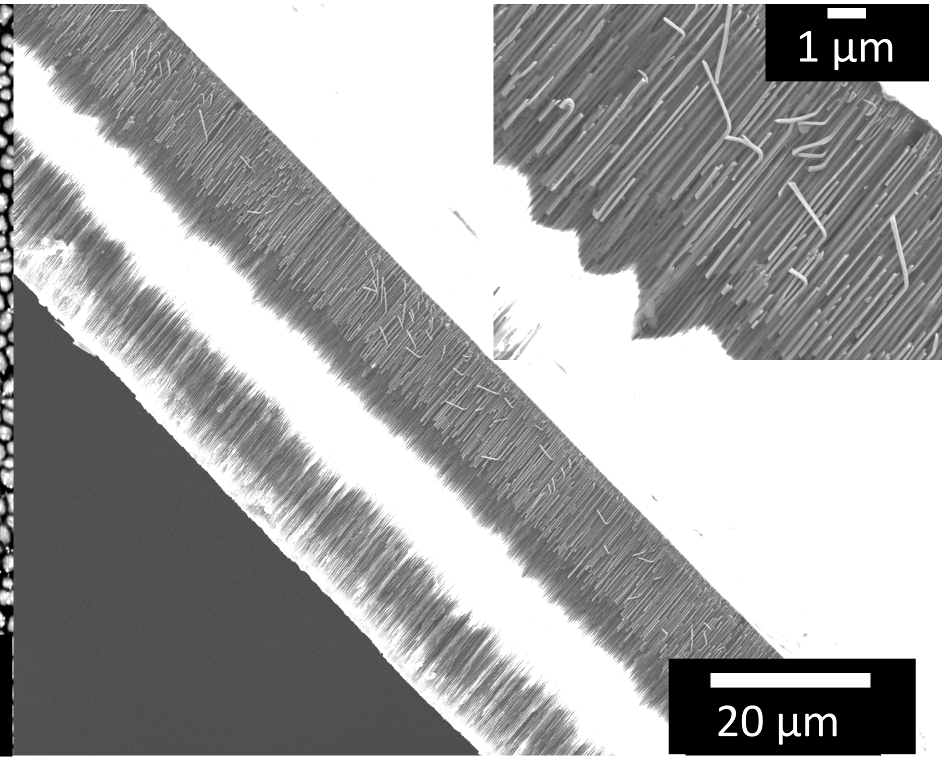




Electrodeposition provides control over the composition, crystallinity, and morphology of the nanowires

Pulsed Deposition of Cu_2Sb Nanowires



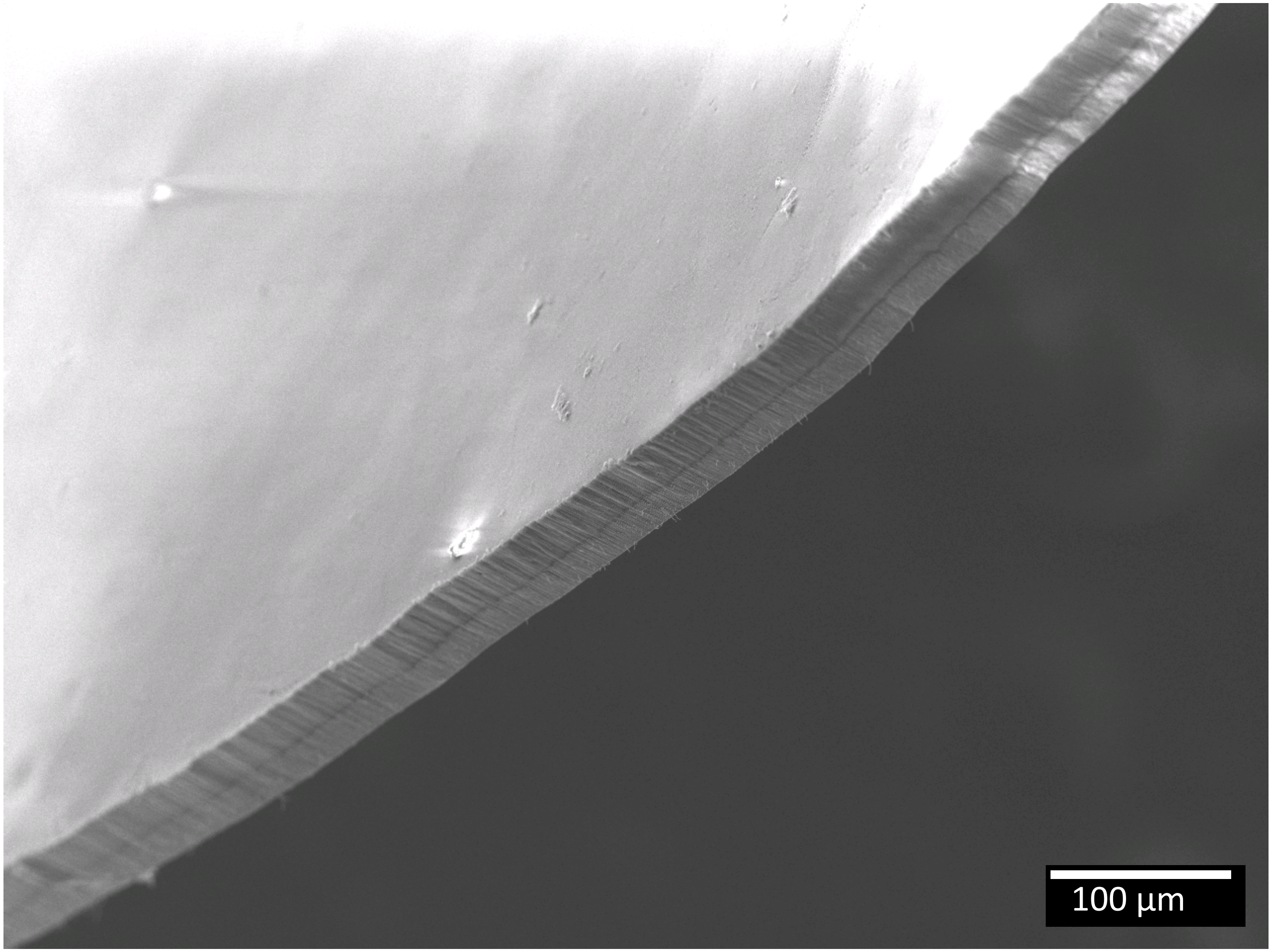


Bottom

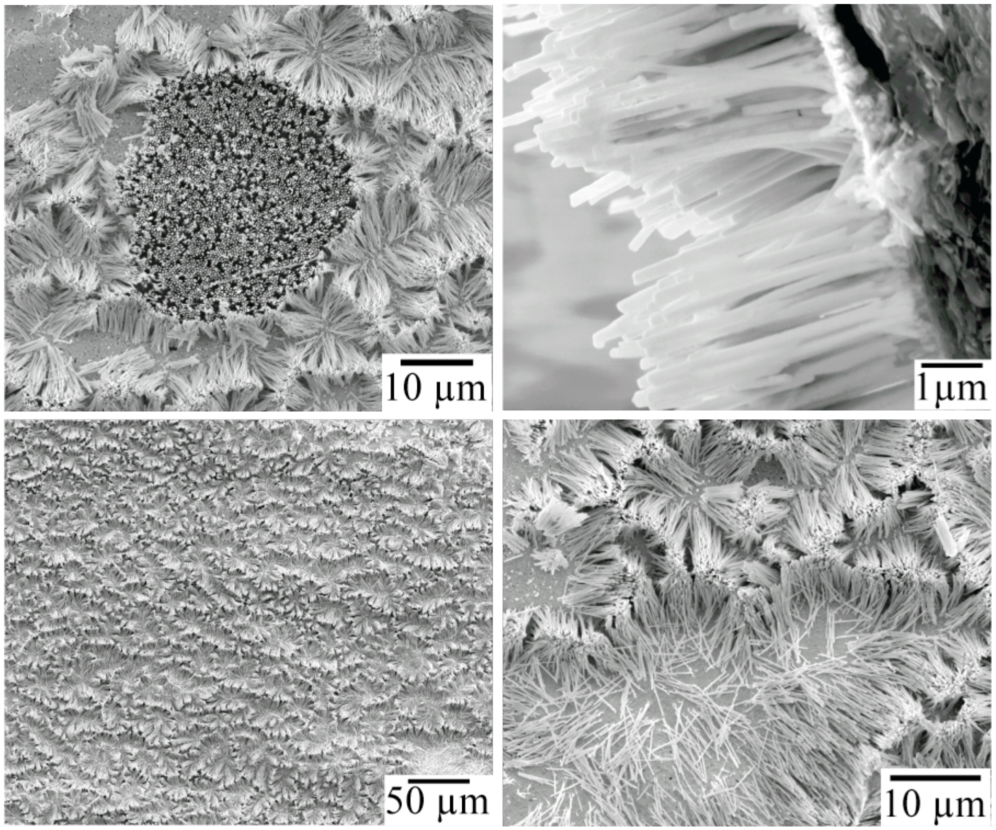
Cross Section

High pore-filling and uniform length

Uniformity Over Long Length Scales

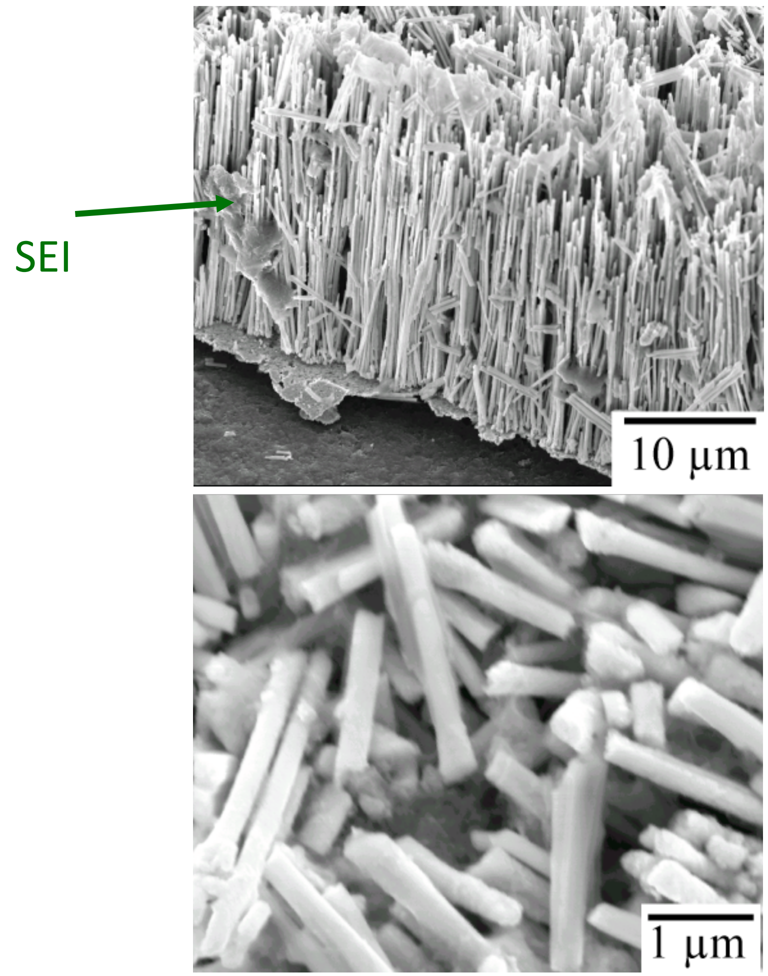


Cycling in Solution

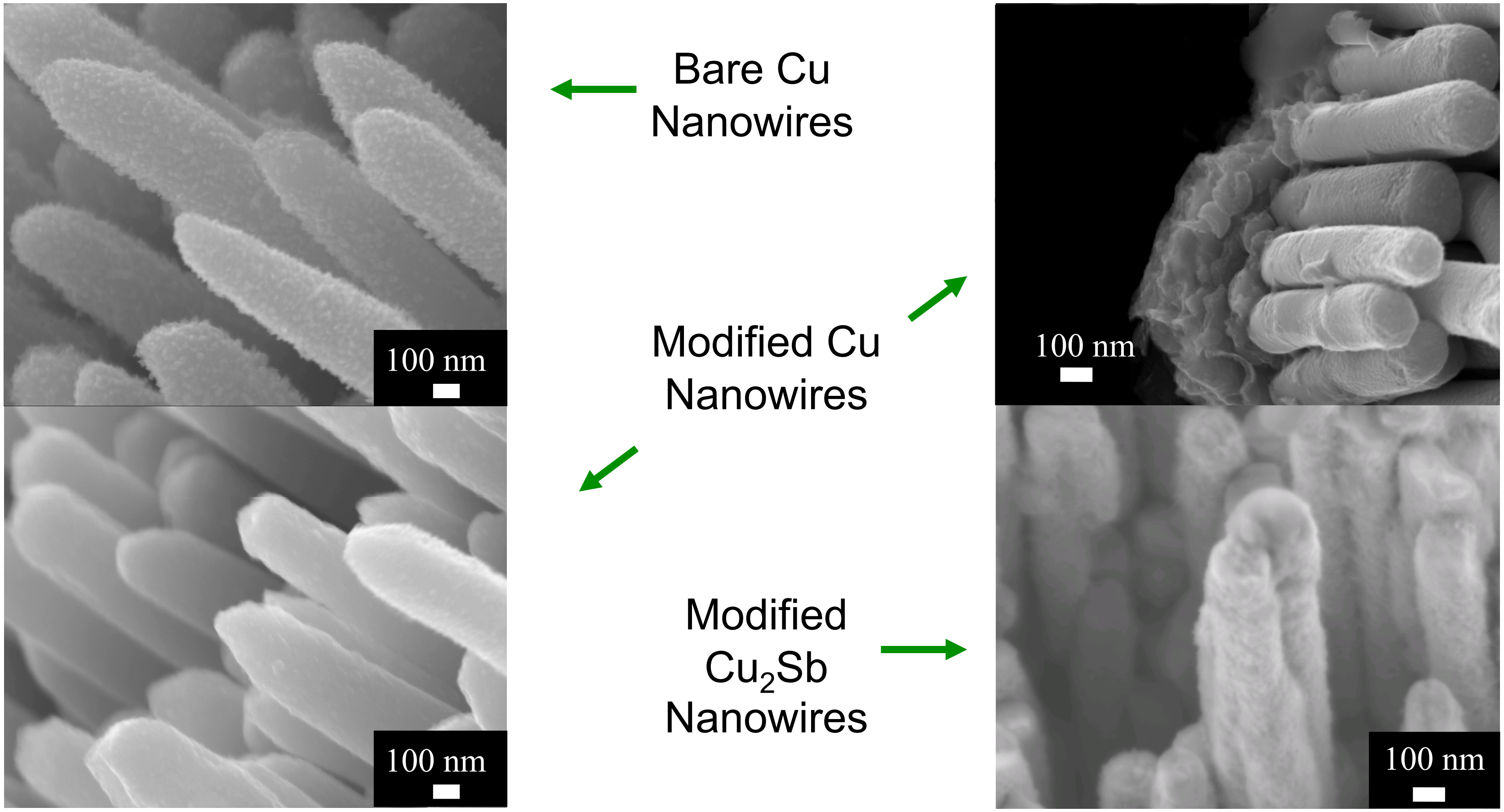


Uniform growth & high density

After 10 cycles



Conformal Coating of Nanowires



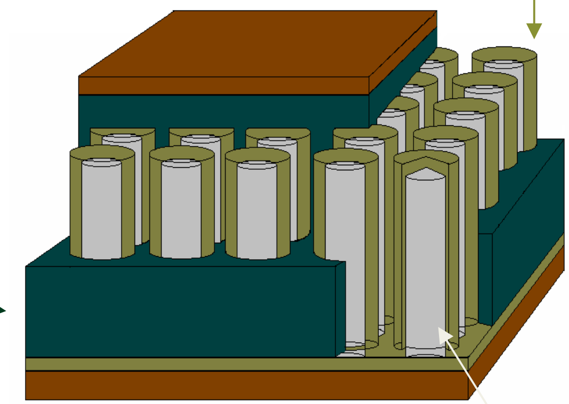
Polymer electrolyte exhibits good adhesion onto Cu_2Sb nanowires

Conclusions and Future Work

Electrolyte:

GYA has been electropolymerized, and shows good ionic conductivity

Cathode



We have coated templates with $LiCoO_2$ and $LiMnO_2$ synthesized using sol-gel methods

Anode:

Cu_2Sb nanowires have been electrodeposited with good crystallinity, high pore filling and uniform wire growth

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Dr. Jennifer Noblitt
Dr. Nick Norberg
Dr. Matthew Rawls
Dr. Shannon Riha
Aaron Wolfe

Prof. Mike Elliott, Prof. Bruce Parkinson

Dr. Chris Rithner, Dr. Pat McCurdy, Dr. Sandeep Kohli

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National Science Foundation
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